

ДОКЛАДЫ  
АКАДЕМИИ НАУК СССР

PROCEEDINGS of the ACADEMY  
of SCIENCES of the USSR

Section: CHEMISTRY

Volume 108, Issues 1-6

May-June, 1956

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

227 WEST 34TH STREET, NEW YORK 10, N.Y.



an agency for the interpretation of international knowledge



ДОКЛАДЫ  
АКАДЕМИИ НАУК СССР

PROCEEDINGS of the ACADEMY  
of SCIENCES of the USSR

Section: CHEMISTRY

Volume 108, Issues 1-6

May-June, 1956

IN ENGLISH TRANSLATION

LIBRARY COPY  
DO NOT REMOVE

CONSULTANTS BUREAU, INC.

333 WEST 57TH STREET NEW YORK 19, N. Y.



an agency for the interpretation of international knowledge

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

Section: CHEMISTRY

Volume 108, Issues 1-6

May-June, 1956

Editorial Board:

Acad. L.A. Artsimovich, Acad. A.G. Betekhtin, Acad. S.A. Vekshinsky,  
Acad. A.N. Kolmogorov (Asst. to Editor in Chief), Acad. A.L. Kursanov,  
Acad. S.A. Lebedev, Acad. I.N. Nazarov, Acad. A. I. Nekrasov,  
Acad. A. I. Oparin (Editor in Chief), Acad. E.N. Pavlovsky, Acad. L.I. Sedov,  
Acad. N.M. Strakhov, Acad. A.N. Frumkin (Asst. to Editor in Chief)

(A Publication of the Academy of Sciences of the USSR)

---

IN ENGLISH TRANSLATION

Copyright, 1957

CONSULTANTS BUREAU; INC.

227 West 17th Street  
New York 11, N.Y.

Printed in the United States

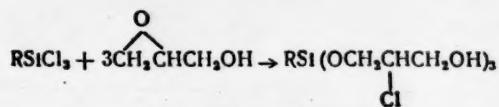
Annual Subscription \$95.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any article in this issue may be purchased from the publisher for \$5.00.

## SYNTHESIS OF ALKYLACETOXYEPOXYSILANES

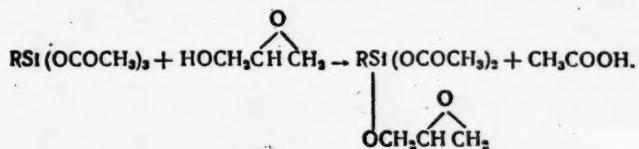
K. A. Andrianov, Associate Member of the Academy of Sciences USSR and V. G. Dubrovina

Reactions of organohalosilanes with ethylene oxide [1, 2] and organochlorosilanes with epichlorohydrin [3] are described in the literature. It has been shown that the reaction proceeds with rupture of the epoxide ring according to



Up to the present, organosilicon compounds containing an epoxide group have not been described. However, the synthesis of such substances is of definite interest, since organosilicon compounds with an epoxide group could be starting materials for the preparation of organosilicon polymers possessing increased adhesion to metals and other materials.

The reaction between alkylacetoxysilanes and glycidol was studied in the present work. It might be expected that rupture of the epoxide ring would not occur during this reaction, since it is known that alkylacetoxysilanes react with alcohols at a relatively low temperature [4]. Moreover, the acetic acid liberated during this reaction acts weakly on the epoxide group. Experiments confirmed this supposition, and showed that the reaction of alkylacetoxysilanes with glycidol proceeds according to the scheme



Methyldiacetoxyepoxypropoxysilane, dimethyldiacetoxyepoxypropoxysilane, dimethylacetoxypepoxypropoxysilane, methylacetoxypepoxypropoxysilane, and vinylacetoxypepoxypropoxysilane were prepared by the indicated reaction. The properties of these compounds are presented in Table 1.

During the study of the reaction it was found that a decrease in the number of acetate groups in the alkylacetoxysilanes hampered their substitution by the glycidol residue. Thus, an acetate group in methyltriacetoxy- and vinyltriacetoxy silane was completely substituted by an apoxypropoxy group, with dimethyl-diacetoxy- and methyldiacetoxysilane the substitution was only 70-75%, and with trimethylacetoxysilane there was, in general, no substitution.

It should be noted that alkylacetoxypepoxypropoxysilanes are hydrolytically and thermally unstable, and analysis of these materials was very difficult.

### EXPERIMENTAL

The following were used as starting materials: methyltriacetoxy-, dimethyldiacetoxy-, trimethylacetoxysilane.

TABLE 1

Substance	Formula	B.p. in °C	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	M <sub>RD</sub>		OCOCH <sub>3</sub> , %		Epoxy group, %	
					Found	Calc.	Found	Calc.	Found	Calc.
Methyldiacetoxypropoxysilane	CH <sub>3</sub> Si(OOCCH <sub>3</sub> ) <sub>2</sub>   OCH <sub>2</sub> —CH—CH <sub>2</sub>   O	84—90 (2 mm)	1.4268	1.1840	50.88	50.72	50.67	50.42	18.25	18.38
Dimethylacetoxypropoxysilane	(CH <sub>3</sub> ) <sub>2</sub> SiOOCCH <sub>3</sub>   OCH <sub>2</sub> —CH—CH <sub>2</sub>   O	70—75 (3 mm)	1.4228	1.1854	45.16	45.41	31.92	31.05	21.51	22.63
Methylacetoxypropoxysilane	CH <sub>3</sub> —Si—OOCCH <sub>3</sub>   H OCH <sub>2</sub> —CH—CH <sub>2</sub>   O	59—67 (3 mm)	1.4230	1.0985	40.80	41.03	33.46	33.52	24.10	24.43
Vinyldiacetoxypropoxysilane	CH <sub>3</sub> —CH—Si—(OCOCH <sub>3</sub> ) <sub>2</sub>   OCH <sub>2</sub> —CH—CH <sub>2</sub>   O	110—115 (4 mm)	1.4302	1.1615	54.77	55.04	46.89	47.96	17.09	17.48

methyl diacetoxyl-, and vinyl triacetoxysilane and glycidol. Methyl triacetoxysilane was prepared by a previously described method [4]. Dimethyl diacetoxyl-, methyl diacetoxyl-, and trimethyl acetoxysilanes were prepared by the action of  $\text{CH}_3\text{COOK}$  on the corresponding alkyl chlorosilanes in a benzene or xylene (in the case of trimethyl acetoxysilane) medium with a yield of 75, 72 and 82%, respectively. According to the literature [5, 6], these compounds have been prepared by the action of  $\text{CH}_3\text{COONa}$  on alkyl chlorosilanes in an ether medium.

Vinyl triacetoxysilane. There is only a mention of the preparation of vinyl triacetoxysilane in the literature [7]. It was synthesized by us in a manner analogous to methyl triacetoxysilane. The yield of the material was 82.2%.

The properties of dimethyl diacetoxyl-, methyl diacetoxyl-, and vinyl triacetoxysilanes are presented in Table 2.

Glycidol. To 830 g (7.5 moles) of glycerol,  $\alpha$ -monochlorohydrin, cooled to 0 degrees, was added over a period of 5 hours to 185 g (3.3 moles) of powdered potassium hydroxide at 5-20 degrees. The mixture was stirred 4 hours at room temperature, after which the KCl was filtered off, and the filtrate was dried with sodium sulfate and twice distilled in a vacuum. 155 g of glycidol was obtained having a boiling point of 50-53 degrees at 5 mm and  $n_D^{20}$  1.4308. 553 g of glycerol  $\alpha$ -monochlorohydrin was recovered. The yield of alcohol, calculated on the chlorohydrin consumed, was 83.9%.

Methyl diacetoxyl epoxypropoxysilane. To 110 g (0.5 mole) of methyl triacetoxysilane was added, with stirring, 37 g (0.5 mole) of glycidol over a period of 30 minutes. The reaction proceeded with the liberation of heat, so that the temperature of the mixture during the introduction of the alcohol was 45-50 degrees. At the end of the introduction of the alcohol, the mixture was stirred for 3 hours at 50 degrees, after which it was distilled under vacuum. 28.9 g of acetic acid was liberated; that is, the reaction proceeded 98.8% to completion. The yield of methyl diacetoxyl epoxypropoxysilane, which distilled at 82-105 deg/3 mm, was 99.8 g, which was 85.2% of theoretical.

Found %:  $\text{OCOCH}_3$  51.01; epoxy group 18.12; C 40.23; H 6.11; Si 11.09  
 $\text{C}_8\text{H}_{14}\text{SiO}_6$ . Calculated %:  $\text{OCOCH}_3$  50.42; epoxy group 18.38; C 41.02; H 5.98; Si 11.96

Mol. wt. (cryoscopically) 238.5.

For  $\text{C}_8\text{H}_{14}\text{SiO}_6$  Mol. wt. calculated 234.1

Repeating the distillation gave a fraction with a b.p. of 84-90 degrees/2 mm;  $n_D^{20}$  1.4268;  $d_4^{20}$  1.1840;  $\text{MR}_D$  found 50.88;  $\text{MR}_D$  calculated for  $\text{C}_8\text{H}_{14}\text{SiO}_6$  50.72.

Found %:  $\text{OCOCH}_3$  50.67; epoxy group 18.25

TABLE 2

Substance	B.p. in °C	$n_D^{20}$	$d_4^{20}$	$\text{MR}_D$		$\text{OCOCH}_3\%$		C, %		H, %		Si, %	
				Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
Dimethyl diacetoxyl-silane	55-56 (7 mm)	1.40-2	1.0523	40.92	41.12	66.89	67.04	10.53	10.91	6.52	6.81	15.12	15.91
Methyl diacetoxyl-silane	62-63 (15 mm)	1.4022	1.0815	36.49	36.75	72.63	72.84	37.49	37.03	6.07	6.17	16.18	17.28
Vinyl triacetoxyl-silane	70-80 (3 mm)	1.4152	1.1478	50.63	50.75	76.57	76.29	41.55	41.38	6.00	5.17	11.06	12.06

Dimethyl acetoxyl epoxypropoxysilane. This compound was synthesized in an analogous manner from 26.4 g (0.15 mole) of dimethyl diacetoxysilane and 11.1 g (0.15 mole) of glycidol. 6.8 g of acetic acid was isolated by distillation of the reaction mixture under vacuum; that is, the reaction proceeded 75.5% to completion. The yield of dimethyl acetoxyl epoxypropoxysilane, which distilled at 66-80 deg/3 mm, was 15.9 g corresponding to 55.9% of theoretical. After repeating the distillation, the fraction boiling at 70-75 deg/3 mm was taken for analysis;  $n_D^{20}$  1.4228;  $d_4^{20}$  1.1854;  $\text{MR}_D$  found 45.16;  $\text{MR}_D$  calculated for  $\text{C}_7\text{H}_{14}\text{SiO}_4$  45.41.

Found %:  $\text{OCOCH}_3$  31.92; epoxy group 21.51; C 43.30; H 7.88; Si 14.27  
 $\text{C}_7\text{H}_{14}\text{SiO}_4$ . Calculated %:  $\text{OCOCH}_3$  31.05; epoxy group 22.03; C 43.31; H 7.96; Si 14.73

Methylacetoxypepoxypropoxysilane. This compound was synthesized from 24.3 g (0.15 mole) of methylacetoxysilane and 11.1 g (0.15 mole) of glycidol. 3.8 g of acetic acid was liberated by distillation under vacuum; that is, the reaction proceeded 75.7% to completion. The yield of methylacetoxypepoxypropoxysilane, which distilled at 58-73 deg/3 mm, was 13.4 g corresponding to 50.8% of theoretical. After repeating the distillation, a fraction boiling at 59-67 deg/3 mm was taken for analysis;  $n_D^{20}$  1.4230;  $d_4^{20}$  1.0985;  $\text{MR}_D$  found 40.80;  $\text{MR}_D$  calculated for  $\text{C}_8\text{H}_{12}\text{SiO}_4$  41.03.

Found %:  $\text{OCOCH}_3$  33.46; epoxy group 24.10; H on silicon 0.50; C 40.36; H 6.67; Si 14.44  
 $\text{C}_8\text{H}_{12}\text{SiO}_4$ . Calculated %:  $\text{OCOCH}_3$  33.52; epoxy group 24.43; H on silicon 0.56; C 40.91; H 6.81; Si 15.90

The hydrogen on the silicon atom was determined by the quantitative liberation of gaseous hydrogen by decomposition of an aliquot with alkali.

Vinyldiacetoxypepoxypropoxysilane. This compound was synthesized from 34.8 g (0.15 mole) of vinyl-triacetoxysilane and 11.1 g (0.15 mole) of glycidol. 8.3 g of acetic acid was liberated by distillation of the reaction mixture; that is, the reaction proceeded 92.2% to completion. The yield of vinyldiacetoxypepoxypropoxysilane, which distilled at 105-124 deg/3 mm, was 23.5 g corresponding to 63.6% of theoretical. After repeating the distillation, the fraction boiling at 110-115 deg/3 mm was analyzed;  $n_D^{20}$  1.4302;  $d_4^{20}$  1.1615;  $\text{MR}_D$  found 54.77;  $\text{MR}_D$  calculated for  $\text{C}_9\text{H}_{14}\text{SiO}_6$  55.04.

Found %:  $\text{OCOCH}_3$  46.89; epoxy group 17.09; C 43.06; H 6.26; Si 10.83  
 $\text{C}_9\text{H}_{14}\text{SiO}_6$ . Calculated %:  $\text{OCOCH}_3$  47.96; epoxy group 17.48; C 43.90; H 6.69; Si 11.32

Determinations of the contents of acetate and epoxy groups were carried out in the following manner: the percentage of acetate groups was determined by titration of an aliquot (0.15-0.25 g) of the material with 0.1 N NaOH, after which the epoxy groups were determined by adding to the contents of the flask 10 ml of pyridine hydrochloride (prepared by mixing 1 liter of pyridine and 16 ml of concentrated hydrochloric acid), boiling the mixture for 20 minutes, and back-titrating the excess hydrochloric acid with 0.1 N NaOH.

Institute of Elementoorganic Compounds  
Academy of Sciences of the USSR

Received October 15, 1955

#### LITERATURE CITED

- [1] R. Sauer, W. Patnode, J. Am. Chem. Soc. 67, 1548 (1945).
- [2] W. Gilliam, R. Meals, R. Sauer, J. Am. Chem. Soc. 68, 1161 (1946).
- [3] K. A. Andrianov, N. N. Sokolov, E. N. Khrustaleva and L. N. Yukina, Bull. Acad. Sci. USSR, Div. Chem. Sci. 531 (1955) (T. p. 469)\*.
- [4] K. A. Andrianov and A. A. Zhdanov, Proc. Acad. Sci. USSR, 94, No. 4, 697 (1954).
- [5] H. Schnyten, G. Weaver, J. Reid, J. Am. Chem. Soc. 69, 2110 (1947).
- [6] A. Bidaud, P. Dumont, French Pat. 950 583 (1949); C. A. 45, 5713 (1951).
- [7] R. E. Scott, K. C. Frisch, J. Am. Chem. Soc. 73, 2599 (1951).

\* T. p. = C. B. Translation pagination.

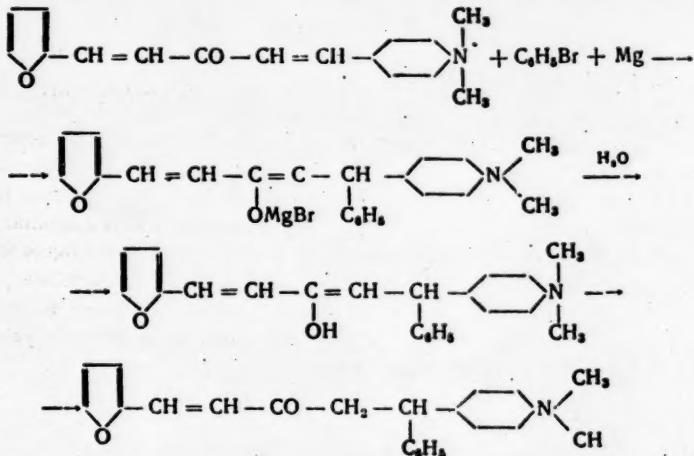
GRIGNARD REACTIONS WITH SOME UNSATURATED KETONES  
CONTAINING A FURAN NUCLEUS

B. N. Dashkevich and S. S. Zhuder

(Presented by Academician I. N. Nazarov, September 26, 1955)

During the carrying out of rough experiments on the introduction of unsaturated ketones containing a furan nucleus into Grignard reactions, we observed that only in rare instances did the reaction proceed normally; usually 1-4 addition of the magnesium halide component occurred; that is, in place of the expected tertiary alcohol, more complex ketones were obtained. In spite of the use of the usual methods for suppressing abnormal reactions, as, for example, carrying out the reaction in a single stage, ketones were formed all the same. We present three examples of such reactions in the present communication, in which are described reactions between unsaturated ketones containing a furan nucleus in the molecule and phenylmagnesium bromide and allylmagnesium bromide. We chose these reactions, because from them we obtained two ketones not described in the literature: 1-furyl-5-phenyl-5-(p-dimethylaminophenyl)-1-penten-3-one and 1, 5-difuryl-1, 7-octadien-3-one, and also we isolated the tertiary alcohol 1-furyl-3-(p-dimethylaminostyryl)-1, 5-hexadien-3-ol.

The reaction between 1-furyl-5-(p-dimethylaminophenyl)-1, 4-pentadien-3-one and phenylmagnesium bromide. We prepared the original ketone by two methods: first, by the condensation of p-dimethylaminobenzaldehyde with furfuralacetone in the presence of an alkali, and, second, by an analogous condensation of furaldehyde with p-dimethylaminobenzalacetone. It melted at 169-170 degrees (with decomposition). The main reaction can be represented as follows:



A mixture consisting of 10 g of the original ketone and 10 g of bromobenzene in ether-benzene solution was added, over a period of 1 hour, to 2 g of magnesium under a layer of absolute ether. At the conclusion of the reaction, the complex formed was a dark red color. The product was decomposed first by ice water and

then by ammonium chloride. Additional ethereal extract from the water layer was added to the separated ether-benzene solution, after which it was distilled up to a temperature of 60 degrees. A yellow precipitate separated out from the remaining part of the solution after cooling; after separation by filtration, the precipitate was washed several times with alcohol and proved to be a satisfactorily pure ketone melting at 113-114 degrees (with decomposition). The yield was 7.5 g or 21.9% based on the bromobenzene.

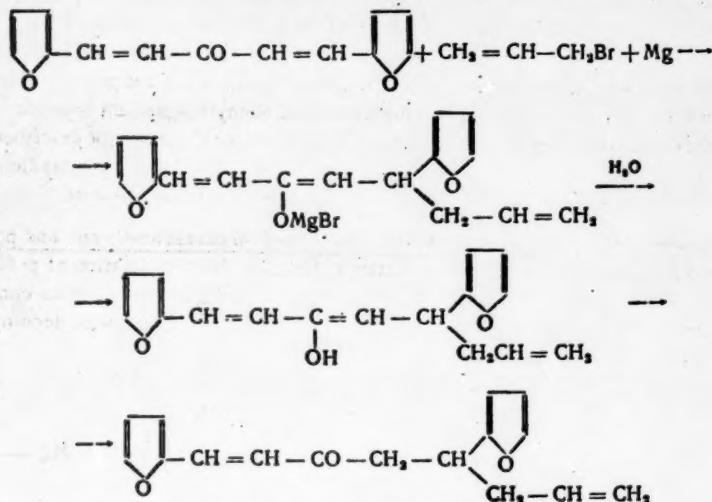
Found %: C 79.11; H 6.76; N 4.26; M 333 (by Rast method)

$C_{13}H_{20}NO_2$ . Calculated %: C 80.00; H 6.66; N 4.05; M 345

As shown by the cited analysis, in this case we obtained a ketone having the structure: 1-furyl-5-phenyl-5-(p-dimethylaminophenyl)-1-penten-3-one. However, we established the presence of traces of a tertiary alcohol in the filtrate after separation of the ketone from the ether-benzene solution. This follows from the fact that the filtrate was turned blue by the action of concentrated acid, the blue color disappearing with the addition of water; that is, it exhibited a property of a halochrome, such as is inherent in an aliphatic-aromatic unsaturated tertiary alcohol [1].

The 2,4-dinitrophenylhydrazone prepared from the ketone melted at 180-181 degrees (with decomposition).

The reaction between difurfuralacetone and allylmagnesium bromide. The original ketone was prepared by condensation of furaldehyde with furfuralacetone in the presence of an alkali hydroxide. It melted at 142 degrees (with decomposition). The main reaction can be represented as follows:



An ether-benzene solution of 5.5 g of difurfuralacetone and 7 g of allyl bromide was added, over a period of 1 hour, to 2 g of magnesium under a layer of absolute ether. The complex formed had a yellow color. It was decomposed first by ice water and then by a solution of ammonium chloride. The ether-benzene solution was separated from the water layer, washed several times with water, and dried over anhydrous sodium sulfate, after which the solvent was distilled off to 1/3 of the original volume. The remaining liquid was of a thick, syrupy consistency and was dark red in color. On the addition of a few drops of water, a yellow precipitate formed. It was purified by solution in methanol and precipitation from the latter with water; the resulting yellow powder was satisfactorily pure ketone with a m.p. of 95-97 degrees and which changed from a yellow color to red during melting. The yield was 3.5 g or 53.34% calculated on the original ketone.

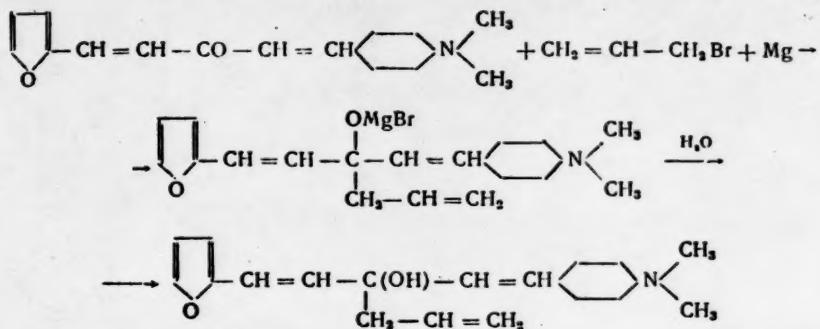
Found %: C 74.64; H 6.26; M 247 (in benzene)

$C_{16}H_{16}O_3$ . Calculated %: C 75; H 6.25; M 256

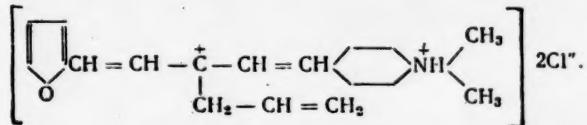
The 2,4-dinitrophenylhydrazone prepared from the ketone melted at 160 degrees (with decomposition).

From the analytical data presented, it follows that we had synthesized 1,5-difuryl-1,7-octadien-3-one.

The reaction between 1-furyl-5-(p-dimethylaminophenyl)-1,4-pentadien-3-one and allylmagnesium bromide. The original ketone in this reaction was the same ketone as in the first reaction described in this communication. This reaction proceeded in two directions—both with the formation of a ketone and with the formation of an alcohol. We were unable to characterize the ketone obtained, since it resublimed rapidly. As regards the alcohol, we were successful in isolating it in the form of the dichloride, and an analysis was carried out on the latter. The reaction for the preparation of the alcohol can be represented as follows:



To 2 g of magnesium under benzene-ether solution was gradually added dropwise 8 g of allyl bromide and, along with this, 4.5 g of the ketone was added in small portions. The complex formed was yellow. It was decomposed as in the preceding cases. The reaction mixture stood for a day, after which the ketone separated as a yellow precipitate. The ether-benzene solution was carefully washed with water, dried with anhydrous sodium sulfate, and distilled at 78 degrees. The dried benzene solution was subjected to the action of methylmagnesium iodide, whereupon methane was liberated, which indicated the presence of alcoholic hydroxyl in the dissolved product. Moreover, by the action of concentrated sulfuric acid the solution was given a brown color which disappeared upon dilution with water, and this is indicative of a halochromic nature arising from the structure of the alcohol. Without liberating the pure alcohol from the benzene solution, we obtained its dichloride by passing dry hydrogen chloride into the solution, as a result of which there was first a precipitation of a light green precipitate and, on continued action of the hydrogen chloride, of a darker gray-green precipitate. After careful washing with absolute alcohol, this precipitate was established as the dichloride of 1-furyl-3-(*p*-dimethylaminostyryl)-1,5-hexadien-3-ol, apparently of the following structure



The yield of the dichloride of the alcohol was 1.5 g or 27.6% calculated on the original ketone. It melted at 90 degrees (with decomposition).

Found %: N 3.68; Cl 19.93 (by Stepanov); M 366.7 (by Rast)  
 $C_{20}H_{23}NOCl_2$ . Calculated %: N 3.84; Cl 19.50 M 364

Thus, as a result of the presence of a furan nucleus in the molecule of the compounds prepared, they were unstable with respect to increased temperature, undergoing resinification below their melting points. As a consequence of the presence of double bonds in the tertiary alcohol prepared, it possessed a halochromic nature.

Uzhgorod State University

Received June 10, 1955

#### LITERATURE CITED

[1] B. N. Dashkevich, *Ukrain. Chem. J.* No. 3 (1955).



THE RELATION BETWEEN THE STRUCTURE AND CERTAIN PROPERTIES  
OF A SERIES OF AZO DYES CONTAINING AMIDE GROUPS

B. M. Krasovitsky, R. M. Matskevich and T. M. Nikishova

(Presented by Academician A. V. Topchiev, October 14, 1955)

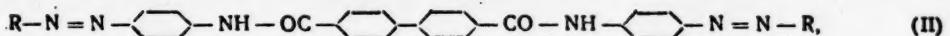
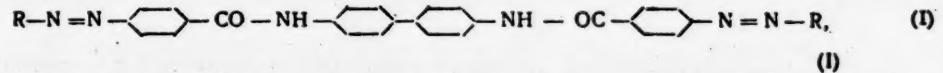
Previously, one of us investigated the relation between structure, color, and substantivity of the simplest azo dyes—the derivatives of benzanilide [1]. The present investigation is devoted to an investigation of dyes containing two amide groups.

Some of the investigated dyes and intermediates required for their preparation have been described, but a part of them were synthesized by us for the first time.

The investigation of the substantivity of the dyes was carried out by the method previously used by us [1]: the dyeing of the calico was carried out for 1 hour at a temperature of 80 degrees. The substantivity value was taken as the amount of dye, in per cent, taken up from the bath during dyeing minus the amount of dye washed out by cold distilled water during washing of the dyed calico to practically colorless wash water.

The absorption maxima of aqueous solutions of the dyes and the color in cellophane were determined by a Goldberg spectrodensograph.

Dyes I and II having the following structure were investigated



where R = the azo component = is H-acid (coupled in alkaline medium).

In structure, these dyes are double molecules of dyes III and IV, which were investigated in the cited work [1].



Besides the benzanilide group, dyes I and II contain a diphenyl nucleus, the basis of benzidine dyes.

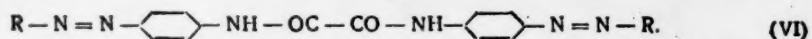
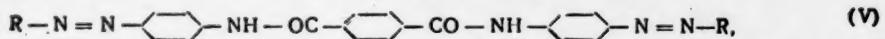
Doubling of molecules III and IV leads to dyes possessing high substantivity (see Table 1).

TABLE 1

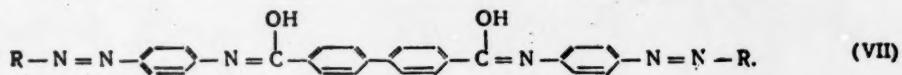
Dye Sensitivity in %	I	II	III	IV	V	VI	VIII	IX	X	XI	XII
	70	67	22	23	68	53	61	32	63	4	10

A comparison of Dyes I and II shows that the difference in their structure (arrangement of the amide groups with respect to the diphenyl nucleus) has almost no effect on substantivity.

It was of interest to compare Dye II with Dyes V and VI, which were prepared from the para-aminoanilides of terephthalic and oxalic acids:

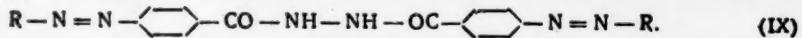
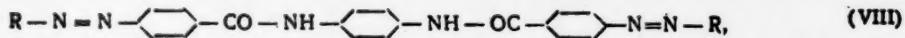


From the data of Table 1 it follows that the substantivities of Dyes V and II, which contain, respectively, one and two benzene rings between amide groups, are approximately equal. The substantivity of Dye VI is somewhat lower. Thus, the introduction of a benzene ring between two  $-\text{CO} - \text{NH} -$  groups leads to an increase in substantivity; further, an accumulation of benzene rings does not increase affinity toward vegetable fibers, although the chain of conjugated double bonds of the imidol form of the dye is lengthened by this:



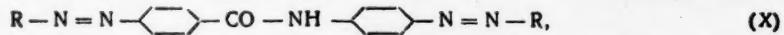
These data conform to the conclusion of B. M. Boroslovsky, who showed that an increase in the number of conjugated double bonds in a chain contributes to an increase in substantivity only up to a certain limit [2].

We also compared the dye from the para-aminobenzoyl derivative of benzidine, I, with dyes from the para-aminobenzoyl derivatives of para-phenylenediamine, VIII, and hydrazine, IX:



As seen from Table 1, Dye IX exhibited considerably less substantivity than the dyes derived from benzidine and para-phenylene-diamine.

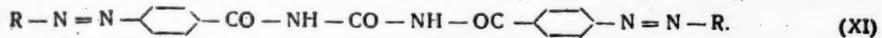
It was of interest to compare the substantivity of Dye X



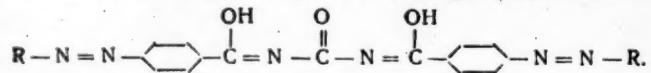
which contains one amide group between the benzene nuclei, with Dyes VI and IX, the molecules of which contain two amide groups directly connected with one another.

Dye VI, which contains two amide groups connected through the carbon atoms, had a somewhat lower substantivity than Dye X (with one amide group); the substantivity of Dye IX, the amide groups of which were connected through the nitrogen atoms, was significantly less than those of Dyes VI and X.

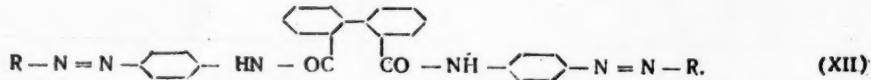
With derivatives of hydrazine, the introduction into the dye molecule of a carbonyl group between the nitrogen atoms, XI, leads to almost complete loss of affinity for vegetable fiber



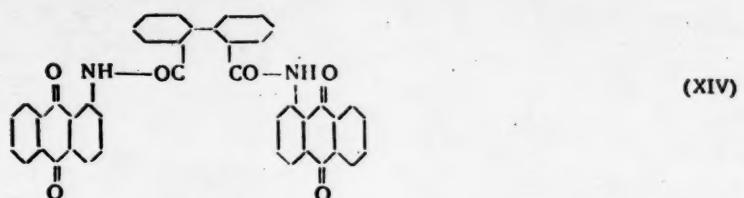
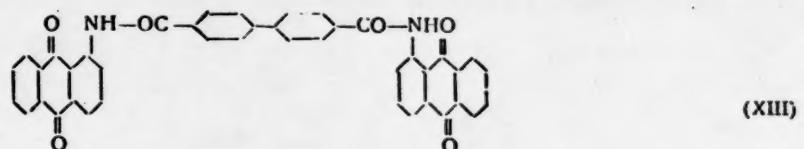
In all probability, the reason for the low substantivity in this case is the absence of a continuous chain of conjugated double bonds even in the imidol form of Dye XI, if it can generally be formed:



Further, we compared Dye II with the isomeric Dye XII



This dye, which was synthesized long ago by one of us, exhibited low substantivity with respect to cotton, and has previously been investigated chiefly as an acid dye [3]. The great difference in substantivity of these two isomeric dyes can be explained, apparently, by steric hindrance arising as a result of the introduction of two bulky substituents in the 2,2'-positions of the diphenyl nucleus. This steric hindrance leads to disruption of the coplanarity of the dye molecule. The shorter chain of conjugated double bonds between amide groups cannot be the cause of the low substantivity of Dye XII, since Dye V — from the para-aminoanilide of terephthalic acid — has a chain of the same length but higher substantivity. It is interesting that a similar rule is observed on comparison of acylaminoanthraquinone Dyes XIII and XIV:



Investigation showed that the selectivity with calico of the leuco form of the first of these dyes during dyeing for 1 hour at a temperature of 50 degrees (in an atmosphere of nitrogen) was 53%, and of the second was 21%.

In Table 2 are presented the absorption maxima of Dyes II, V, VI, X and XII.

The dye with one amide group gave a deeper color in aqueous solution than all other dyes, giving a somewhat deeper color than the dye from the aminoanilide of oxalic acid, which contained two directly connected amide groups; the appearance of a benzene ring between these groups leads to a further increase in color; the introduction of a second benzene ring between the amide groups does not exhibit an effect on the depth of color. Finally, the dye from the para-aminoanilide of diphenic acid, in which there is steric hindrance, had the highest color.

There was a still greater difference in the color of these dyes in cellophane. While the dyes which were derivatives of benzoin, diphenyl-4,4'-dicarboxylic, terephthalic, and oxalic acids had considerably deeper color in cellophane than in aqueous solution, Dye XII gave close to the same absorption maxima in solution and in cellophane. In all probability, this dye, owing to non-coplanarity of structure, had less conjugation in the molecule, and, as a consequence of this, the formation of the deeply colored imidol form was hindered.

N. F. Kuryshko participated in the experimental part of the work.

A. M. Gorky Kharkov State University

Received October 13, 1955

#### LITERATURE CITED

- [1] B. M. Krasovitsky, B. I. Ostrovskaya and D. G. Pereyaslova, Proc. Acad. Sci. USSR 106, No. 1, 72, (1956) (T. p. 106)\*
- [2] B. M. Boroslovsky, Doctorate Dissertation, Moscow, 1946 (cited by F. I. Sadov, P. P. Viktorov et al. Chemical Technology of Fibrous Materials, Moscow, 1952, p. 377).
- [3] B. M. Krasovitsky and E. S. Khotinsky, Ukrains. Chem. J. 18, 490 (1952).

\* T. p. = C. B. Translation pagination



## SYNTHESIS OF ISOPROPYLNAPHTHALENE AND SECONDARY BUTYLNAPHTHALENE BY THE ALKYLATION OF NAPHTHALENE WITH OLEFINS

Academician A. V. Topchiev, Ya. M. Paushkin and M. V. Kurashev

At the present time, alkylnaphthalenes find wide use both in the pure form and in the synthesis of various products having important significance in the national economy. Among the more important of such products are: synthetic oil; pourpoint depressants for lubricating oils; surface active materials. Work has been carried out in an investigation of the possible use of alkylnaphthalenes as raw material for the production of synthetic rubber of the butadiene-styrene type [1-3].

Sulfuric acid, aluminum chloride, and certain other compounds have been used as catalysts for the alkylation of naphthalene. These catalysts are subject to a number of shortcomings, chief among which are high corrosivity and relatively low yields of alkylate.

Our investigations of the alkylation of benzene with olefins using a catalyst based on orthophosphoric acid and boron fluoride [4-7] showed that, with this catalyst, it is possible to obtain, in high yield, a high quality alkylate — with a high content of monoalkylbenzenes. In connection with this, an investigation was carried out on the alkylation of naphthalene, dissolved in carbon tetrachloride, with propylene and n-butene using a complex of orthophosphoric acid and boron fluoride as the catalyst.

The experiments on the alkylation of naphthalene with olefins were carried out in a 1-liter glass reactor fitted with a stirring device, a thermometer, a reflux condenser, and a capillary for the addition of olefin. Temperature variation during the experiments did not exceed 2-3 degrees. Pure naphthalene, with a m.p. of +80 degrees, was used for the reactions; the olefins were prepared by catalytic dehydration of the corresponding alcohols over activated aluminum oxide, and had a purity of about 99%. The liquid reaction products, after separation from the catalyst layer, were washed with water, a 20% solution of sodium hydroxide, again with water, dried over calcined calcium chloride, and, after distilling off the solvent, they were distilled in a vacuum column having 22 theoretical plates. The results of the investigation are presented in Tables 1 and 2. The content of isopropylnaphthalene (260-265 degree fraction) and of sec-butylbenzene (275-280 degree fraction) in the broad, 200-260 degree fraction (naphthalene fraction) was evaluated from the melting point of the fraction; for this purpose, a curve relating experimentally determined melting points of mixtures of alkylnaphthalenes with naphthalene to the content of the components was constructed. In our case, it was possible to use such a method, since other reaction products were practically absent (see Figure 1). The solidification temperature of the 200-260 degree fraction from propylene alkylation was +62.5 degrees, and from butene alkylation +61.5 degrees, which corresponded to contents in the 200-260 degree fraction of 29.5%  $C_{10}H_7C_3H_7$  (260-265 degree fraction) and 28.6%  $C_{10}H_7C_4H_9$  (260-290 degree fraction). A check of this method by molecular weight determinations showed a discrepancy between the methods of less than 1%.

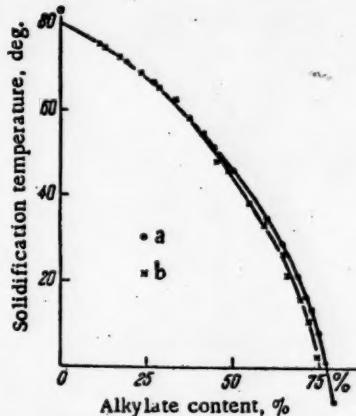


Figure 1. Dependence of the solidification point of naphthalene on its alkylate content.  
a) 260-290 degree fraction (sec-butyl-naphthalene);  
b) 260-265 degree fraction (isopropylnaphthalene).

During the course of the experiments, the effects of olefin-addition rate, amount of catalyst, temperature, and naphthalene:olefin mole ratio on the course of the reaction were investigated.

TABLE 1

Alkylation of Naphthalene with Propylene by Means of an Orthophosphoric Acid Boron Fluoride Complex

Experiment No.	Reaction temperature, °C	Olefin-addition rate, hours <sup>-1</sup>	Molc ratio	Amount of ca- talyst %	Yield of fractions in % of theoretical				Total con- tent 260- 265° frac- tion in - alkylate
					260- 280°	Above 280°	260- 265°, isopro- pynaphtha- lene		
1	50	20	2:1	10	83	11	62	87	
2	50	20	2:1	15	84	11	64	88	
3	50	20	2:1	30	84	10	64	89	
4	50	20	2:1	35	85	10	65	89	
5	50	20	2:1	15	84	22	64	82	
6	50	60	2:1	15	83	11	63	88	
7	50	100	2:1	15	80	13	60	86	
8	25	20	2:1	15	82	11	64	87	
9	80	20	2:1	15	87	9	65	90	
10	95	20	2:1	15	91	6	69	94	
11	50	20	1:1	15	66	13	50	74	
12	50	20	2:1	15	84	10	64	88	
13	50	20	4:1	15	94	4	70	95	
14	50	20	6:1	15	95	4	71	96	

It was established that the yield of monoalkylnaphthalenes increased and that of polyalkylnaphthalenes decreased with an increase in temperature. Thus, for example, the propylation of naphthalene at 25 degrees gave 62% of theoretical of isopropynaphthalene (260-265 degree fraction) and 11% of theoretical of polyisopropynaphthalene; at 95 degrees, the values for these fractions were 69 and 6%, respectively. In the butylation of naphthalene at 25 degrees, the yields of the reaction products sec-butyl naphthalene (260-290 degree fraction), sec-butyl-naphthalene (275-280 degree fraction), and poly-sec-butyl naphthalene (fraction boiling above 290 degrees) were, respectively, in per cent of theoretical: 83, 64; at 80 degrees, 88, 68, 8.

The amount of catalyst had an effect only on an increase in its concentration from 10 to 15%, a further increase in concentration had practically no effect on the reaction (Experiments Nos. 1, 2, 3, and 4). A change in the olefin-addition rate from 20 to 100 hours<sup>-1</sup> (Experiments Nos. 4, 5, 6, and 7) decreased the yield of monoalkylnaphthalene and increased the yield of polyalkylnaphthalene during propylation, respectively, from 64 and 11% to 60 and 13%, and during butylation from 67 and 9% to 52 and 22%.

An increase in the naphthalene:olefin mole ratio had a noticeable effect on the product composition. Thus, for example, the yield of sec-butyl naphthalene at a naphthalene:butylene ratio of 1:1 was 58% of theoretical, 66% at 2:1, and 72% at 4:1; corresponding to this there was a decrease in the yield of poly-sec-butyl naphthalene (fraction boiling above 290 degrees) from 14 to 9 to 4%, respectively. A similar rule was also observed in the alkylation of naphthalene with propylene (Table 1, Experiments Nos. 11, 12, and 13). Mono-, di-, tri-, and tetraisopropynaphthalene were found in the alkylate produced at a naphthalene:propylene mole ratio of 1:1, and the mono-, di-, and tri-isomers were found at a ratio of 2:1.

The butene alkylate apparently contained only mono- and di-sec-butyl naphthalene. Compositions of alkylates produced at various naphthalene:olefin mole ratios are presented in Table 3. Although an increase in the naphthalene:butene ratio caused an increase in the yield of monoalkylnaphthalenes; nevertheless, the

process should be carried out at decreased ratios not exceeding 2:1, since in an adverse case a naphthalene-alkylnaphthalene mixture with a m.p. of the order of +60 degrees is obtained, and separation of the alkylate from it presents considerable difficulty.

TABLE 2

Alkylation of Naphthalene with n-Butene by Means of an Orthophosphoric Acid-Boron Fluoride Complex

Expt. No.	Reaction temp. °C	Olefin-addition rate, hours <sup>-1</sup>	Mole ratio	A mount of catalyst, %	Fraction yield (% theoreti.)			Total content of 260-280° fraction in alkylate
					260-290°	Above 290°	275-280° sec-butyl-naphthalene	
1	50	20	2:1	10	84	10	65	89
2	50	20	2:1	15	87	9	67	91
3	50	20	2:1	30	87	9	67	91
4	50	20	2:1	35	87	9	67	91
5	50	30	2:1	15	85	10	65	89
6	50	60	2:1	15	79	14	61	85
7	50	100	2:1	15	67	22	52	75
8	25	20	2:1	15	83	11	64	88
9	50	20	2:1	15	86	9	66	91
10	80	20	2:1	15	88	8	68	92
11	50	20	1:1	15	76	14	58	85
12	50	20	2:1	15	86	9	66	91
13	50	20	4:1	15	94	4	72	96
14	50	20	6:1	15	95	3	73	97

TABLE 3

Content of Alkylnaphthalenes in Naphthalene-Alkylnaphthalene Mixtures.

Component	Naphthalene-butene		Mol. wt.	Sp. gr.	Refractive index	Bromine no.
	1:1	2:1				
	Composition in %					
Naphthalene	21.0	45.5	—	—	—	—
Isopropylnaphthalene	67.0	47.7	170	0.9775	1.5786	—
Diisopropylnaphthalene	9.5	6.3	212	0.9684	1.5718	—
Triisopropylnaphthalene	1.2	0.5	252	0.9597	1.5604	—
Tetraisopropylnaphthalene	0.7	—	289	—	—	—
Residue above 330 degrees	0.6	—	367	0.8874	1.5230	26
Naphthalene	10.6	43.2	—	—	—	—
Sec-butylnaphthalene	76.0	52.1	185	0.9762	1.5818	—
Di-sec-butylnaphthalene	12.6	4.7	240	0.9548	1.5593	—
Residue above 330 degrees	0.8	—	350	0.9235	1.5365	22

The physicochemical constants of the products were determined, and are presented in Table 4.

TABLE 4

Properties of Naphthalene-Alkylation Products

Alkylation product	Mol. wt.	Sp. gr.	Refractive index	B. p. °C	Viscosity
Isopropylnaphthalene	{ 171 169	0.9835 0.9798	1.5835 1.5763	260-280 260-265	-23.4 5.75 -36 5.40
Literature data	170	0.9795	1.5784	263-264	- -
Sec-butylnaphthalene	{ 185 184	0.9736 0.9762	1.5824 1.5818	260-290 275-280	-22 7.89 -31.7 7.44
Literature data	184	0.97	1.5814	147/33 mm	- -

The results of the investigation of the alkylation of naphthalene with butenes show that the orthophosphoric acid-boron fluoride complex is a highly efficient catalyst for this reaction.

Institute of Petroleum  
Academy of Sciences of the USSR

Received November 14, 1955

#### LITERATURE CITED

- [1] Yu. S. Zalkind and I. A. Arbuzova, Plastics 3, 249 (1939).
- [2] J. C. Ghosh, Petroleum 13, 283 (1950).
- [3] J. E. Nickels, B. B. Corson, Ind. Eng. Chem 43, 1685 (1951).
- [4] A. V. Topchiev, M. V. Kurashev and Ya. M. Paushkin, Proc. Acad. Sci. USSR 91, No. 5 (1953).
- [5] M. V. Kurashev, A. V. Topchiev and Ya. M. Paushkin, Proc. Acad. Sci. USSR 107, No. 6 (1956) (T. p. 203 )\*
- [6] A. V. Topchiev, M. V. Kurashev and Ya. M. Paushkin, Proc. Acad. Sci. USSR 107, No. 5 (1956). (T.p. 191 )\*
- [7] A. V. Topchiev and Ya. M. Paushkin, Compounds of Boron Fluoride as Catalysts in Alkylation, Polymerization, and Condensation Reactions, 1949.

\* T. p. = Consultants Bureau Translation pagination.

## THE STRUCTURE OF AGAR-AGAR GEL

V. I. Sharkov and R. K. Boyarskaya

(Presented by Academician V. A. Kargin, October 17, 1955)

Up to the present time, the nature of swollen gels of linear high polymers remains obscure. Several hypotheses to explain the structure of these gels have been presented. Thus, for example, A. V. Dumansky [1], S. M. Lipatov [2], N. I. Peskov [3], Gerngross, Hofmeister, Dyuklo and others consider swollen gels as two-phase systems composed of a continuous network structure filled with the liquid dispersed medium. Depending on the nature of the gel, the dispersed medium can consist of pure solvent or a solution containing a low molecular fraction of the substance from which the network structure is constructed. Gelation of a sol is explained by coalescence of thread-like micelles existing in the solution at the moment of gelation. By micelle, in this case, is meant a cluster of linear macromolecules disposed in parallel, which, at the ends of the micelles, form a fringe which contributes to the linking of the micelles on conversion of the sol to a gel.

On the other hand, V. A. Kargin [4], Pauli and others consider swollen gels as single-phase systems in which the dissolved macromolecules weld together at separate points forming a molecular three-dimensional network filled with the dispersed medium. Such an explanation of the structure of gels follows from the concept of solutions of high polymers as true solutions. In view of the obscurity of the question, we attempted to apply the method of fractional hydrolysis to the investigation of the nature of such gels and sols.

In previous investigations [5], we showed that the rate of hydrolysis of a typical linear high polymer — cellulose — changed sharply depending on the course of the reaction under homogeneous or heterogeneous conditions. In these experiments, the rate of hydrolysis of a homogeneous solution of cellulose was 70-100 times greater than the rate of hydrolysis of the same cellulose in the undissolved state. During these measurements, all the remaining parameters having an effect on the rate of hydrolysis were constant. This property of linear polysaccharides can be used to clarify the homogeneous and heterogeneous nature of gels and sols, it being assumed that in single-phase gels and sols the macromolecules of high polymers are hydrolyzed many times faster than in the case of a two-phase structure. Hence, by observing the rate of hydrolysis of a polysaccharide which forms a true or micellar solution, certain conclusions can be made as to one or the other structure.

We have investigated various polysaccharides by this method. Below are presented the results of its use for the investigation of sols and gels of agar-agar. As is well known, the latter is composed, for the most part, of linear polysaccharides which, upon quantitative hydrolysis, form galactose. On this basis, the rate of hydrolysis of agar-agar in our experiments was determined by determining the amount of sugar formed. The yield of sugar was expressed in per cent of the maximum yield of sugar on quantitative hydrolysis of the agar-agar. The latter was obtained by the method of Kizel and Semiganovsky for difficultly hydrolyzable polysaccharides, and proved to be 70%. Experiments on the comparative hydrolysis of agar-agar were carried out in 10% sulfuric acid. The agar-agar sols were prepared by mixing an aqueous solution of agar-agar and sulfuric acid at the appropriate temperature (above 80 degrees), whence, as a result of the mixing, a solution containing 10% sulfuric acid and the desired amount of agar-agar was obtained.

The solutions prepared in this manner, even when containing 10% agar-agar, did not gel at ordinary temperatures, and were turbid, mobile sols which showed no signs of stratification. The agar-agar gels were prepared in water, and then were aged, at ordinary temperature, in frequently changed, cold 10% sulfuric acid until all the free water in the gel had been replaced by 10% acid. From 6 to 8 hours were usually required for this. Observations showed that such treatment had no effect on the stability of the prepared gels. 20 g of 2-mm diameter pieces of gel saturated with acid were placed in a 100-milliliter, round-bottomed flask fitted with a reflux condenser and a thermometer; 50 ml of pre-heated 10% acid was then introduced, and the mixture, with careful stirring, was quickly brought to the assigned temperature. Temperature was maintained with a precision of  $\pm 1$  degree. At the conclusion of this hydrolysis, the mixture was quickly cooled,

allowed to stand for 3 hours for equalization of concentration in the pieces of gel and in the surrounding solution, and then a sample of the liquid was taken for analysis of sugar content.

For investigation by the described method, 5% sols in 10% sulfuric acid were prepared and subjected to hydrolysis at temperatures of from 50 to 100 degrees. The sols were prepared by quickly mixing 10% solutions of agar-agar in boiling water with 20% sulfuric acid, the temperature of which was so chosen that the mixture was at the assigned temperature. The results of the experiments can be seen in Figure 1A.

Inspection of this figure shows that, at all temperatures investigated, hydrolysis of the polysaccharide proceeded rapidly in the first 40 minutes, after which it slowed down sharply. The amount of easily hydrolyzed fraction of the polysaccharide in agar-agar was variable and depended on the temperature of the solution. The higher the temperature of the solution, the greater the percentage of easily hydrolyzed agar-agar polysaccharide in the sol. This phenomenon can be explained as being due to the occurrence of the polysaccharide in the external homogeneous agar-agar sol in two different states: easily and difficultly hydrolyzable. The relationship between these states is not constant and changes with the solution temperature. The higher the temperature, the more of the easily hydrolyzable polysaccharide that is formed in the solution.

It is possible to explain this phenomenon of the simultaneous existence in the sol of homogeneously dissolved polysaccharide macromolecules and colloidal micelles on the basis of the above cited considerations. With an increase in temperature, the micelles are gradually broken down into individual macromolecules which form a homogeneous solution.

An approximate idea of the dependence of the ratio of molecularly dissolved to micellar agar-agar polysaccharide on temperature of the investigated sol can be obtained from Figure 1B.

Completely different results were obtained during the hydrolysis of 5% and of absolutely dry agar-agar gels under the same conditions. In this series of experiments, the hydrolysis of agar-agar was carried out at different temperatures and for a constant time of 60 minutes. The yields of sugar obtained are presented in Figure 2. A curve for the 60-minute hydrolysis of an agar-agar sol is presented in this same figure. Comparison of the curves shows that the amount of easily hydrolyzed component depends, not only on the temperature, but also on the colloidal state of the agar-agar. At temperatures above 80 degrees, that is, above the liquefaction point of the gels, all three curves, corresponding to sol and gel states, coincide. The curves diverge below this temperature, and the divergence increases with decreasing temperature. In distinction from the sol, the agar-agar gel contains significantly less easily hydrolyzable component which indicates an increased content of tightly packed micellar particles. The least amount of easily hydrolyzable material was observed in the pre-dried agar-agar gel. This experiment showed that the structure of agar-agar gel depends on the temperature at which it exists, the relative percentage of micellar fraction continuously increasing with decreasing temperature.

The different content of easily hydrolyzable component in gel and sol can also be seen in Figure 3, where the results of hydrolysis of a sol, a gel, and a pre-dried gel at 50 degrees are presented. Under these experimental conditions, the gel was not broken up, but retained the form of the original pieces. The curves presented in the figure show that the easily hydrolyzable component in the gel, also, was practically completely hydrolyzed in the first 60 minutes. Past 60 minutes, the rate of hydrolysis dropped off sharply in spite of the considerable amount of unhydrolyzed polysaccharide remaining. Analogous curves were obtained by us at other temperatures. The retention of the gel structure after removal of the easily hydrolyzable component indicates that the gel skeleton, welded out of individual micelles into a continuous three-dimensional network, is of a heterogeneous form.

Interesting results were obtained by the application of this method of investigation to agar-agar gels of different concentrations. In this series of experiments, agar-agar gels of 0.5, 1.0, 2.0, 5.0 and 10.0% concentration were prepared in water, and the water in them was then replaced by 10% sulfuric acid. The gel samples prepared by this method were hydrolyzed for 60 minutes at 50 degrees. The results obtained are presented in Figure 4. Experiments on the hydrolysis of agar-agar sols of the same concentrations were carried out under the same conditions at the same time. The results obtained are also presented in Figure 4. A comparison of the curves obtained shows that, in sols of the same concentration, the ratio of easily and difficultly hydrolyzable fractions of polysaccharides is almost constant which indicates the relative stability of micelles in solution. In gel, on the contrary, this ratio was not constant. The lower the concentration of the gel, the greater the amount of easily hydrolyzable component in it. However, even in 0.5% gel, 60% of the polysaccharide still

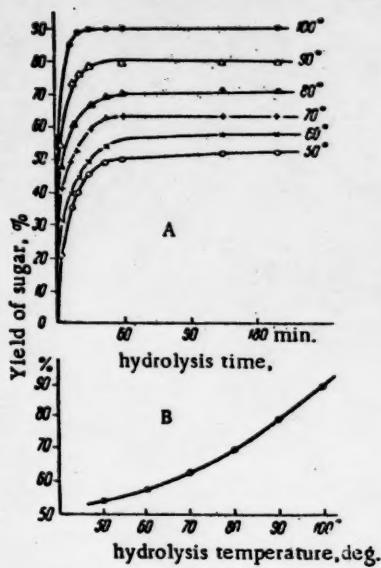


Figure 1. Yield of sugar during hydrolysis of 5% agar-agar sol in 10% sulfuric acid.  
A) at different temperatures and different reaction times; B) at different temperatures and a hydrolysis time of 3 hours.

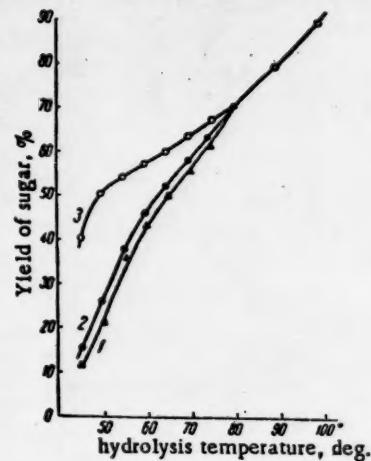


Figure 2. Comparative data on the yield of sugar during hydrolysis of agar-agar gels and sols.  
Hydrolysis time, 60 minutes.  
1) Dry gel; 2) gel; 3) solution.

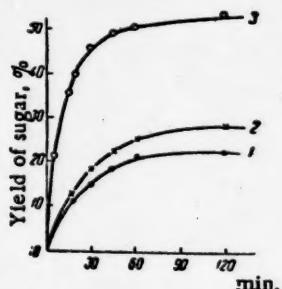


Figure 3. Yields of sugar during hydrolysis of 5% agar-agar gels and sols. Temperature, 50 degrees.  
1) Dry gel; 2) gel; 3) solution.

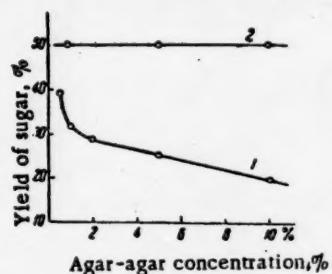


Figure 4. Yields of sugar during hydrolysis of agar-agar gels and sols of different concentrations.  
1) Gel; 2) solution.

occurs in the micellar state. In order to clarify the question of the reversibility of such structures, we subjected diluted agar-agar gels to slow drying. The resulting gels of increased agar-agar concentration were compared for hydrolyzability with gels of the same concentration prepared in the usual manner. These experiments showed that the slightly dried and the specially prepared gels of equal concentration gave practically the same yield of sugar upon hydrolysis. Thus, for example, 1% agar-agar gel at 50 degrees in 10% sulfuric acid gave, in 60 minutes, 31.64% sugar. This same gel, dried to a content of 2% dry material, gave 29.61% sugar under the same conditions, and the specially prepared 2% gel gave 29.0-29.3% sugar. Thus, the relative amount of easily hydrolyzable component is decreased by drying the gel; the amount of difficultly hydrolyzable material is increased.

All-Union Research Institute  
for the Hydrolysis and Sulfite-Alcohol Industry

Received September 28, 1955

#### LITERATURE CITED

- [1] A. V. Dumansky, *The Study of Colloids*, 1948, p. 371 and others.
- [2] S. M. Lipatov, *The Physical Chemistry of Colloids*, 1948.
- [3] N. I. Peskov and E. M. Aleksandrova-Preis, *Course in Colloid Chemistry*, 1948, p. 310 and others.
- [4] V. A. Kargin, *Reports of the First and Second Conferences on High Molecular Compounds*, Acad. Sci. USSR Press, 1945, p. 60, 85.
- [5] V. I. Sharkov, V. S. Muromtseva and G. Ya. Paramonova, *J. Appl. Chem.* 21, 103, 109 (1948); V. I. Sharkov, *Hydrolysis Ind.* 3, No. 4, 5 (1950); V. I. Sharkov, *Coll. The Chemistry and Physical Chemistry of High Molecular Compounds*, Acad. Sci. USSR Press, 1952, p. 132.

## CERTAIN REGULARITIES DURING THE THERMAL CHLORINATION OF n-DODECANE

R. S. Galanina and A. S. Nekrasov

(Presented by Academician A. V. Topchiev, October 27, 1955)

In previous work [1-4], we carried out an investigation of the chlorination of straight chain hydrocarbons of the methane series containing from 6 to 11 carbon atoms, inclusive, which were isolated from petroleum.

In further work, we carried out experiments on the thermal chlorination of normal dodecane isolated from the kerosene fraction of petroleum. The work was directed toward a study of certain kinetic regularities of the chlorination reaction and toward the determination of the physicochemical constants of dodecane chloro derivatives. There are no data in the literature on the chlorination of dodecane.

The reaction was carried out vapor phase in a previously described flow system [4]. The normal dodecane subjected to chlorination was isolated from petroleum by extractive crystallization with urea; its physical constants were: m. p. 216°, density 0.7588, refractive index 1.4222, and molar refraction 57.7.

The experiments were carried out under conditions guaranteeing maximum yield of monochloride. It was established previously that basic conditions for the production of monochloride are an excess of hydrocarbon and minimum contact time.

With the aim of clarifying the effect of temperature on the degree of chlorination of the hydrocarbon and on the rate of the chlorination reaction, experiments were conducted at various temperatures. The results of the experiments are presented in Table 1.

TABLE 1

Effect of Temperature on Yield of Monochloride

Reaction temperature, in °C	Yield of monochloride, in %	Yield of dichloride, in %	Chlorine consumption, in %
280	98.8	1.2	100
260	96	4	100
250	80	8	85
240	62	10	78

TABLE 2

Effect of an Excess of Hydrocarbon on Yield of Reaction Products. Reaction Temperature 280°, Space Rate 25 liters/liter/hour

Excess of hydrocarbon	Yield of monochloride, in %	Yield of dichloride, in %
10-fold	98.5	1.2
8 "	98	2
6 "	96.5	3.5
4 "	95	5

The reaction of chlorine with dodecane proceeds very vigorously. A small amount of heat is required for the initial activation of the molecules. The reaction rate increases rapidly with an increase in temperature. If heat liberated by the reaction cannot be equally distributed throughout the mass of reactants, local overheating results, leading to ignition. Therefore, an excess of hydrocarbon and high space rates are required for the normal course of the reaction. The optimum temperature for the chlorination of dodecane is 280°. In this case, the yield of monochloride comprises 98.8% and that of dichloride comprises 1.2%.

An excess of hydrocarbon has a substantial effect on the rate of chlorination of n-dodecane and on the completeness with which it is chlorinated to the monochloride. In an investigation of this question, experiments were conducted at various mole ratios of hydrocarbon to chlorine. The results of the experiments are presented in Table 2.

The experiments showed that maximum yield of monochloride occurred at a 10-fold excess of hydrocarbon. The chlorine was completely consumed. The reaction proceeded smoothly. With a decrease in the excess to 6- and 4-fold, ignition was observed.

TABLE 3

Effect of Space Rate on Product Yield in the Chlorination of n-Dodecane. Reaction Temperature 230°. 10-Fold Excess Hydrocarbon

Space rate, liters/liter/hour	Monochloride yield in %	Dichloride yield in %
25	98.8	1.2
20	98	2
16	96.5	3.5
12	95	5

in the chlorination of dodecane. In this case, the monochloride yield comprises 98.8%, dichloride yield is 1.2%. Free chlorine is not present in the reaction products. The effect of space rate on the degree of chlorination of the molecules is shown in Table 3. The monochloride fraction, boiling at 220-250° was distilled in a fractionating column having an efficiency of 40 theoretical plates. Primary chlorododecane, boiling at 241-244°, and secondary monochlorodecanes, boiling at 231-238°, were separated by the distillation. The monochlorides obtained were investigated. Density, refractive index, and chlorine content were determined, and the molar refraction was calculated. The constants are presented in Table 4.

TABLE 4

Physicochemical Constants of Monochlorodecanes

Monochloride	Yield, %	B. p. °C	$d_4^{20}$	$n_D^{20}$	MRD	Chlorine content, %
Primary	48	241-244	0.8600	1.4420	62.94	17.78
Secondary	52	231-238	0.8655	1.4390	62.12	17.52

Knowing that the dodecane molecule contains 6 hydrogen atoms bonded to primary carbons and 20 atoms bonded to secondary carbons, the relative activity of the hydrogen atoms in the dodecane molecule toward substitution by chlorine can be calculated using the formula previously proposed by us [4]. The relative value characterizing the activity of the primary hydrogen atoms is 3.08.

Crimean Affiliate of the  
Academy of Science UkrSSR Simferopol

Received October 25, 1955

#### LITERATURE CITED

- [1] R. S. Galanina, Proc. Acad. Sci. USSR, 88, No. 6, (1953); 91, No. 4, (1953).
- [2] R. S. Galanina and A. S. Nekrasov, Ukr. Chem. J., 21, 2 (1955)
- [3] R. S. Galanina and A. S. Nekrasov, Ukr. Chem. J., 21, 3 (1955)
- [4] R. S. Galanina and A. S. Nekrasov, Proc. Acad. Sci. USSR, 100, No. 4, (1955).

**VERIFICATION, BY MEANS OF TAGGED ALCOHOL, OF THE DEHYDRATION-CONDENSATION MECHANISM OF THE FORMATION OF HYDROCARBON CHAINS IN THE SYNTHESIS OF HYDROCARBONS FROM CO AND H<sub>2</sub>**

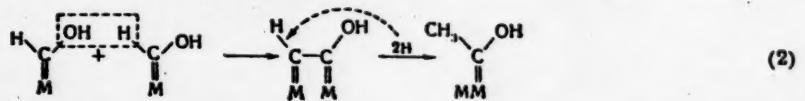
O. A. Golovina, Associate Member of the Academy of Sciences,  
USSR S. Z. Roginsky, M. M. Sakharov and Ya. T. Eidus

Until recently, the majority of investigators postulated the intermediate formation of methylene radicals in the synthesis of hydrocarbons from CO and H<sub>2</sub> over metallic catalysts. Along with this postulation, it was assumed that the hydrocarbon skeleton was formed by polymerization of methylene radicals [1].

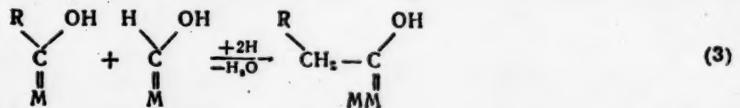
Recently, this radical-polymerization scheme of the formation of hydrocarbon chains has been opposed by the dehydration-condensation scheme [2], the complex initially forms, approximating the structure of methyl alcohol



and the hydrocarbon chain grows as a result of a dehydration-type of condensation and hydrogenation:



or in the general case



Kummer and Emmet attempted to show the correctness of the latter scheme by experiments in which tagged alcohols were added to the synthesis gas [3].

Since the results of Kummer and Emmet were based on a comparatively small number of experiments carried out only with iron catalysts, which are not typical catalysts for the production of hydrocarbons at atmospheric pressure, and also in view of internal contradictions in the work of the cited authors, it seemed important to carry out an analogous radiochemical investigation on cobalt catalysts, which are more typical for the synthesis of hydrocarbons at ordinary pressure.

A cobalt catalyst, on which a considerable part of the work of Ya. T. Eidus and N. D. Zelinsky [4] was carried out, was used in the present work. In order to obtain a better comparison of the results with those of the cited work [4], we essentially reproduced the conditions and methods of this work.

The experiments were carried out with a mixture of  $1\text{CO}:2\text{H}_2$  at a temperature of  $195^\circ$  and a space rate of 100 liters/liter/hour. The tagged ethyl alcohol, which was added to the feed gas, had a radioactivity of 8.4 mc/mole. Just as in the Kummer and Emmet experiments, the specific radioactivity of the hydrocarbons obtained decreased with an increase in molecular weight, while the molar radioactivity of the  $\text{C}_6\text{-C}_{29}$  hydrocarbons remained practically constant. The average molar radioactivity of the  $\text{C}_6\text{-C}_{29}$  hydrocarbons was 18 times less than the molar radioactivity of the original alcohol. From this it follows that, on the average, only  $1/18$  of the hydrocarbons of any molecular weight (exclusive of the light hydrocarbons) were formed from the alcohol introduced into the reaction. In contrast to the results of Kummer and Emmet, our radioactivity, not only of methane, but also of the  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  hydrocarbons was appreciably less than the average molar radioactivity of the  $\text{C}_6\text{-C}_{29}$  hydrocarbons. Thus, the main result of the American investigators (constant radioactivity for the majority of the hydrocarbons) was confirmed for a cobalt catalyst also, and it, probably, is typical for the Orlov-Fischer-Tropsch synthesis. It should be noted that our data differ substantially from the data of the American investigators with respect to the radioactivity of methane. According to Kummer and Emmet, the molar radioactivity of methane comprised only 1-7% of the average molar radioactivity of the hydrocarbons produced, while ours comprised 29%.

The literature data and our radiometric data can scarcely be explained without the concept of the growth of a physical chain, if not for the basic case, then for any case of a parallel synthesis route. It is possible that our coefficient 18 represents the number of physical chains initiated with the absorption of an alcohol molecule. However, a more precise activity balance is lacking for confirmation of the conclusion. In other words, on a cobalt catalyst there are physical chains of up to  $n-1$  members, where  $n$  is the number of carbon atoms in the hydrocarbon molecules, and, apparently, there are also reaction chains with the repetition number 18. By such a route, each physical chain is one link in the reaction chain.

The radiometric data confirm the first link in the scheme of Ya. T. Eidus and N. D. Zelinsky, which is the formation of a hydroxymethylene complex. The constancy of the ratio  $\frac{\rho_{\text{hydrocarbon}}}{\rho_{\text{alcohol}}}$  ( $\rho$  - is molar radioactivity) for various values of  $n$  is most easily explained by unity of the mechanism of chain formation with the direct participation of the added alcohol (or any active products of its conversion) and the mechanism without such participation. However, this conclusion is not completely confirmed, and it requires additional verification. In connection with this, note that participation of the alcohol, not in initiation, but in breaking away the physical chains could also lead to the results described by Kummer and Emmet and by us.

Notwithstanding the opinion of the American investigators, neither the data of the cited work nor our data provide sufficient basis for refutation of the methylene scheme and confirmation of the dehydration-condensation scheme, since methylene radicals could participate in the growth of chains initiated by the alcohol or formed from the latter, and it still remains to be proved that parallel formation of hydrocarbons without the participation of the introduced alcohol does not proceed through methylene radicals. The dehydration-condensation scheme is presented by us as being more probable for catalysts of isosynthesis ( $\text{Al}_2\text{O}_3$ ,  $\text{ThO}_2$ ), which belong to the acid-base type and which actively catalyze dehydration processes; this has already been noted in the literature [5].

Institute of Physical Chemistry and N. D. Zelinsky  
Institute of Organic Chemistry, Academy of Sciences,  
of the USSR

Received November 5, 1955

#### LITERATURE CITED

- [1] V. A. Karzhavin, Prog. Chem., 16, 327 (1947).
- [2] H. Storch, N. Golumbic and R. Anderson, The Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen, Foreign Lit. Press, (The U. S. Title for this book is: The Fischer-Tropsch and Related Syntheses) 1954 (Translation).
- [3] J. T. Kummer, H. H. Podgurski et al., J. Am. Chem. Soc., 73, No. 2, 564 (1951); J. T. Kummer and P. H. Emmet, J. Am. Chem. Soc., 75, No. 21, 5177 (1953).

[4] Ya. T. Eidus and N. D. Zelinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 2, 289 (1940); No. 1, 45 (1942); No. 4, 190 (1942); Ya. T. Eidus, Prog. Chem., 19, No. 1, 32 (1950).

[5] Ya. T. Eidus, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 1024 (1953) (T. p. 913)\*

---

\* T. p. - C. B. Translation pagination.



## THE EFFECT OF ANIONS OF THE OUTER SPHERE ON THE NATURE OF SUBSTITUTION INTO THE INNER SPHERE OF COMPLEX COMPOUNDS

Associate Member of the Academy of Sciences, USSR, A. A.  
Grinberg and Kh. I. Gildengershel

As early as 1915, L. A. Chugaev, in his classical work on pentammines of tetravalent platinum [1], emphasizing the role of the  $\text{PO}_4^{3-}$  ion as a precipitant in the phosphate method of synthesis, expressed the opinion that its effect was possibly not limited just to this.

I. I. Chernyaev and A. N. Fedorova [2] pointed out the important role of the sulfato group in the synthesis of pentammines of tetravalent Pt and also of mixed hexammines of the composition  $[\text{Pt}(\text{NH}_3)_4\text{En}] (\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ . They assumed that unrestricted acceptance of the principle of trans-influence leads to dependence of the stability of inner sphere substituents on the nature of the groups found in the outer sphere.

The low degree of dissociation of the mixed hexammine  $[\text{Pt}(\text{NH}_3)_4\text{En}] (\text{SO}_4)_2$ , established by I. I. Chernyaev and Khorunzhenkov [3], and also of the mixed pentammine  $[\text{PtEn}(\text{NH}_3)_3 \cdot \text{Cl}]_2 (\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$  into ions confirms the idea of Chernyaev on the selective ability of pentammine and hexammine ions to bond stably to the sulfato group (in contrast to  $\text{NO}_3^-$  and  $\text{Cl}^-$ ).

Studying the absorption of ammines of cobalt and chromium, Linhard [4] established that, in a solution of the luteo salt, the equilibrium  $[\text{Co}(\text{NH}_3)_6]^{3+} + \text{I}^- \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$ , was established, strongly displaced in the direction of the ion  $[\text{Co}(\text{NH}_3)_6]^{2+}$ .

Thus, in this case there was association with monovalent anions. It was also established that, with a large excess of anion, there were undissociated molecules of  $[\text{Co}(\text{NH}_3)_6]_3$  in the solution.

The effect of the concentration and nature of the outer sphere anion on the rate of substitution into the inner sphere was established by Plane and Taube [5], who studied the exchange reaction  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} - \text{H}_2\text{O}$ , and also by Taube and Posey [6], who investigated the transformation of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$  into  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^{2+}$ . The latter investigators established that the equilibrium state of  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{SO}_4^{2-} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{SO}_4]^{2+} + \text{H}_2\text{O}$  did not depend on the concentration of  $\text{SO}_4^{2-}$  in the broad interval of 0.02 to 2.6 M.

Analyzing the experimental data, the authors were led to the conclusions: 1) that there is present in such a system an association product of the outer sphere anion with the complex cation  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \text{SO}_4^+$  which is converted into a sulfato-ion according to  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \text{SO}_4^+ \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{SO}_4]^{2+} + \text{H}_2\text{O}$ , and 2) that an increase in the concentration of the  $\text{SO}_4^{2-}$  ion accelerates to an equal extent, substitution into the inner sphere of the ions  $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}] \text{SO}_4 \text{SO}_4^+$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^{2+}$ ; that is, it accelerates the process of the transfer of the  $\text{SO}_4^{2-}$  ion from the inner sphere to the outer.

In 1949, the authors of the present article attempted to use the specific effect of the outer sphere sulfato group for the synthesis of mixed hexammines of the composition  $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4(\text{NH}_3)_2]\text{Cl}_4$  and  $[\text{Pt}(\text{CH}_3\text{NH}_2)_4(\text{NH}_3)_2]\text{Cl}_4$  [7]. In the course of these experiments, it was observed that, in place of the expected mixed hexammines, the hexammine cation  $[\text{Pt}(\text{NH}_3)_6]^{4+}$  was formed.

Thus, a new method for the synthesis of hexammines of tetravalent platinum was found, which boiled down to the following operations: 1) the action of ammonia and a large excess of ammonium sulfate on the salt  $[\text{Pt}_4\text{Cl}_2]\text{Cl}_2$ , where  $\text{L} = \text{C}_2\text{H}_5\text{NH}_2$ ; 2) solution of the resulting mixed chlorosulfate hexammine  $[\text{Pt}(\text{NH}_3)_6] \text{SO}_4 \text{SO}_4^+$ .

\* En = ethylenediamine.

$\text{Cl}_{4-2x}(\text{SO}_4)_x$  in a concentrated solution of  $\text{NaOH}$  and precipitation of the  $\text{SO}_4^{2-}$  ion with the calculated amount of  $\text{BaCl}_2$ ; 3) addition to the filtrate, after separation of the precipitated  $\text{BaSO}_4$ , of an excess of hydrochloric acid.

As a result, as was shown, the hexammine chloride of the composition  $[\text{Pt}(\text{NH}_3)_6\text{Cl}_4 \cdot \text{H}_2\text{O}$  was formed.

Since then, this reaction, which is of interest not only from the preparational point of view, has been subjected to further study with the aim of determining its mechanism.

It has been established that :

- 1) The ion  $[\text{Pt}m_4\text{Cl}_2]^{2+}$ , where  $m = \text{CH}_3\text{NH}_2$ , reacts analogously to the ion  $[\text{Pt}_4\text{Cl}_2]^{2+}$ .
- 2) Mixed tetrammines of the general formula  $[\text{Pt}m_4-x \text{ a}_x \text{ Cl}_2]\text{Cl}_2$  (where  $a = \text{NH}_3$ ) also react if  $x$  is within the limits of 1 to 3.
- 3) The Groh salt  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$ , which genetically approaches the salt  $[\text{Pt}(\text{NH}_3)_6\text{Cl}_4]$ , under these same conditions of treatment does not give the hexammine.

In the reaction of the Groh salt with ammonia in the presence of a large excess of ammonium sulfate there is formed the hydroxypentammine sulfate, which, as stated above, can be converted into the corresponding chloride.

4) In the process of the above-mentioned synthesis there occurs partial saponification of the ethylamine molecule bound in the inner sphere to ammonia, which remains bound to the platinum, and to ethyl alcohol [8].

Further, we wanted to establish to what extent the described reaction depended on the specificity of the sulfato group.

In this connection, it was decided to substitute the  $\text{PO}_4^{3-}$  ion for the  $\text{SO}_4^{2-}$  ion. If this were successful, synthesis of hexammines would be appreciably simplified, since it would be possible to eliminate the rather troublesome operation of removing the  $\text{SO}_4^{2-}$  ion by means of  $\text{BaCl}_2$ .

The results of the attempt to substitute the  $\text{PO}_4^{3-}$  ion for the  $\text{SO}_4^{2-}$  ion are described in the present article.

The system of synthesis in the cases described below was as follows. A sample of the initial tetrammine ( $\sim 1 \text{ g}$ ) was treated with a solution of  $2.5 - 3 \text{ g}$  of  $(\text{NH}_4)_2\text{HPO}_4$  in  $10 \text{ ml}$  of water and  $10 \text{ ml}$  of a concentrated solution of  $\text{NH}_3$ . The mixture was boiled for  $0.5 - 1$  hour over an open flame and then heated for  $2 - 3$  hours on a water bath. Periodically, during each half hour,  $5 - 7 \text{ ml}$  of a concentrated solution of ammonia was added. As a result of this treatment a white precipitate was formed, which, after separation from the mother liquor, dissolved readily in several drops of hydrochloric acid solution. The addition of an excess of concentrated hydrochloric acid to this solution resulted in the formation of a white crystalline precipitate. The precipitate was washed with alcohol and with ether, and was subjected to analysis.

It was shown that, by the use of the Groh salt  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$  as the initial tetrammine, the Chugaev salt  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$  was obtained under the stated conditions. The yield was  $0.6 \text{ g}$ .

Analytical data on the preparations obtained by repeating the synthesis three times are :

Found %: Pt 1) 46.45; 2) 46.40; 3) 46.41; 4) 45.96; Cl 1) 33.75; 4) 33.81  
 $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ . Calculated %: Pt 46.24; Cl 33.60

On reaction with  $\text{KI}$ , the substance gave a characteristic graphite-form precipitate of  $[\text{Pt}(\text{NH}_3)_4\text{I}_2]\text{I}_2$ , and the action of  $\text{NaOH}$  on a relatively concentrated solution liberated a characteristic yellow precipitate according to the equation  $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3 + \text{NaOH} \longrightarrow [\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]\text{Cl}_2 + \text{NaCl} + \text{H}_2\text{O}$ .

By the action of a mixture of  $\text{NH}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  on the methylamine analog of the Groh salt  $[\text{Pt}m_4\text{Cl}_2]\text{Cl}_2$ , in spite of a long reaction time, we were unable to isolate even an amount sufficient for analysis.

Thus, a sharp distinction has been noted in the action of the ions  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  on these two tetrammines.

Actually, by using a Groh salt as the starting material we obtained different products - chloropentammine and hydroxopentammine, respectively, and in both cases the reaction proceeded very readily.

In the case of the methylamine analog of the Groh salt, which, in the presence of  $\text{SO}_4^{2-}$  ion, very readily forms the ion  $[\text{Pt}(\text{NH}_3)_6]^{4+}$ , upon the use of  $\text{PO}_4^{3-}$  ion everything went into solution, from which, as already noted, nothing was isolated.

The reaction of the complex tetrammines with  $\text{NH}_3$  in the presence of  $\text{PO}_4^{3-}$  ion led to the formation of products the analysis of which indicated them to be a mixture of pentaminine and hexammine.

With the addition of ammonia or  $\text{NaOH}$  to the resulting products, a characteristic yellow precipitate was formed, which, by the analytical data and properties, was easily identified as the amidochlorotetrammine  $[\text{Pt}(\text{NH}_3)_4\text{NH}_2\text{Cl}]Cl_2$ .

It was interesting that the yield of solid phase appreciably increased on changing from  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]Cl_2$  (0.17 g) to  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]Cl_2$  (0.35 g) and, further, to  $[\text{Pt}(\text{NH}_3)_3\text{Cl}_2]Cl_2$  (0.48 g) calculated on the basis of 1 g of starting material.

This was conformably placed in the series with the tetrammines  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]Cl_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]Cl_2$ , with the first of which the yield of solid phase under these same conditions was insignificantly small and with the second of which it was 0.6 g.

Only once were we successful in preparing the pure hexammine, and then in very small yield, by the use of the tetrammine  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]Cl_2$ .

Summarizing, it can be said, first, that our data once again emphasize the effect of outer sphere anions on the course of substitution into the inner sphere of the complex cation, and, second, that different substitution products can arise under the influence of different outer sphere anions.

Received October 31, 1955

#### LITERATURE CITED

- [1] L. A. Chugaev, Bull. Inst. for the Study of Platinum, No. 4, 3 (1926).
- [2] I. I. Chernyaev and A. N. Fedorova, Bull. Inst. for the Study of Platinum, No. 8, 73 (1931).
- [3] I. I. Chernyaev and S. I. Khorunzhenkov, Bull. Inst. for the Study of Platinum, No. 8, 83 (1931).
- [4] M. Linhard, Z. Electrochem., 50, 224 (1944).
- [5] R. A. Plane and H. Taube, J. Phys. Chem., 56, 33 (1952).
- [6] H. Taube and F. A. Posey, J. Am. Chem. Soc., 75, 1463 (1953).
- [7] A. A. Grinberg and Kh. I. Gildengershel, J. Appl. Chem., 10, 1053 (1949).
- [8] A. A. Grinberg and Kh. I. Gildengershel, Proc. Acad. Sci. USSR, 101, 491 (1955).



## THE QUESTION OF THE MECHANISM OF VULCANIZATION ACCELERATORS.

### REACTION OF MERCAPTOBENZOTHIAZOLE WITH SULFUR

B. Dogadkin and I. Tutorsky

(Presented by Academician A. A. Balandin, November 4, 1955)

The investigation of the reaction of sulfur with mercaptobenzothiazole (Captax, MBT) is of great interest from the point of view of clarifying the mechanism of the action of the latter as a vulcanization accelerator. We studied the reaction of MBT with elemental sulfur in the melt and in solvent media — vaseline oil and xylene. The course of the reaction was followed by means of the  $H_2S$  liberated, which was removed from the reaction medium by a continuous stream of nitrogen and was absorbed in a solution of  $CdCl_2$ .

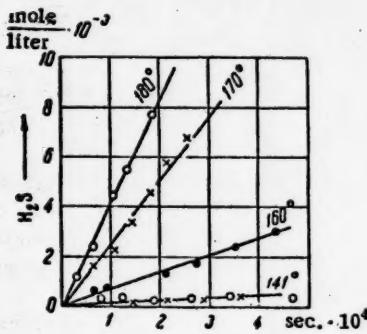


Fig. 1. Kinetics of the liberation of  $H_2S$  on heating sulfur and MBT at various temperatures in a vaseline oil medium.

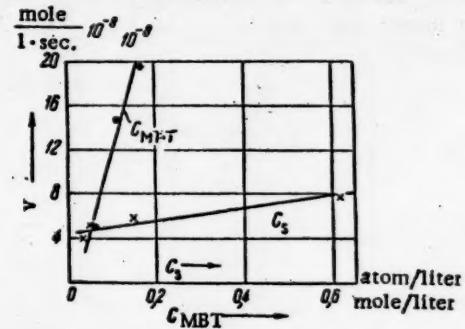


Fig. 2. Dependence of the rate of  $H_2S$  liberation on the concentration of sulfur ( $C_s$ ) and MBT ( $C_{MBT}$ ).

In Figure 1 are presented the kinetics of the liberation of  $H_2S$  on heating the mixture in a medium of vaseline oil, the concentration of MBT and sulfur comprising, respectively, 0.06 moles/liter and 0.655 g-atoms/liter. This ratio and concentration of reactants correspond to those in the vulcanization of rubber. As can be seen, the splitting out of  $H_2S$  under the stated conditions proceeds at a constant rate, which can be explained by the very insignificant change in concentrations of reactants over the entire time (only 1.3% of the MBT introduced reacted in 10 hours at 140°). The kinetics of the liberation of  $H_2S$  from a melt of MBT and sulfur at 140° practically coincide with the kinetics of the reaction in solution (see Figure 1). The temperature dependence of the rate constants leads to the expression  $K = 3.54 \cdot 10^{10} e^{3350/RT}$ .

The reaction proceeds analogously in a xylene medium at the boiling point ( $\approx 138^\circ$ ). The only difference consisted of some excess of liberated  $H_2S$  in comparison with the reacting MBT. Meanwhile, control experiments showed that, under the stated conditions, neither sulfur nor MBT separately reacted with xylene. Splitting of hydrogen from a molecule of the latter occurred only on the joint action of sulfur and MBT, that is, as a result of reaction with those intermediate compounds (free radicals) formed by the interaction of sulfur and MBT.

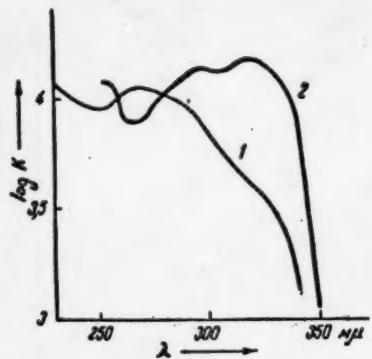


Fig. 3. Absorption spectra of dibenzothiazolyl disulfide (1) and conversion products of MBT (2).

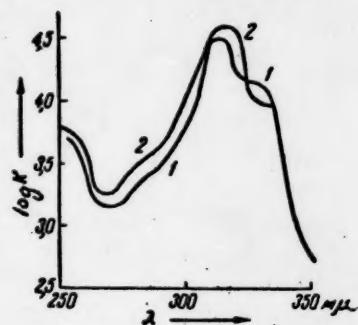


Fig. 4. Absorption spectra of conversion products of MBT extracted with NaOH after reaction with sulfur: 1) in mixture with rubber; 2) in the melt.

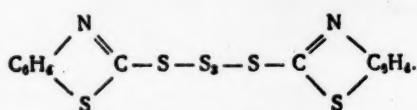
In Figure 2 are presented data characterizing the change in the rate  $v$ , of the liberation of  $H_2S$  with a change in the concentration of reactants. From these data it is seen that the reaction rate increased linearly with an increase in the total concentration of sulfur and MBT. However the ratio  $v/C$ , where  $C$  is concentration, increased with an increase in the concentration of MBT (see Table 1) and decreased with an increase in the concentration of sulfur. The latter phenomenon can be explained by the absorption by the sulfur, under the conditions of the reaction, of SH radicals forming compounds of the type  $HS-S_x-SH$  [1]. With an increase in the concentration of sulfur (above a certain limit), there is an increase in the amount of SH groups.

TABLE 1

MBT concentration, in moles/liter	S concentration, in g-atoms/liter	Rate constant, sec <sup>-1</sup> · 10 <sup>5</sup>
0.06	0.0318	13.4
	0.0655	7.5
	0.157	4.0
	0.627	1.01
0.0595		8.3
0.119	0.0655	13.0
0.179		11.3

The kinetics of the liberation of  $H_2S$  are greatly accelerated by the introduction of stearic acid (an activator for the vulcanization process) into the reaction mixture, and they are completely suppressed by oxides of nitrogen. The latter fact can be considered as indirect evidence of the radical mechanism of the interaction of sulfur and MBT.

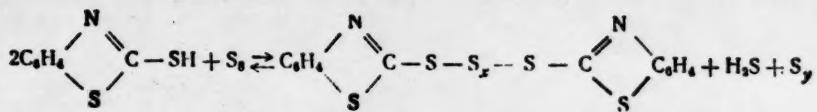
As a result of the reaction, MBT is converted into a polysulfide of the elemental composition: C, 37.94%; S, 52.5%; N, 6.05%; and H, 2.69%, which corresponds to the average formula



M. p. (with decomposition)  $\approx 130^\circ$ . The absorption spectrum of the polysulfide\* (see Figure 3) has a maximum in the region of  $330 \text{ m}\mu$ , which is characteristic of linear polysulfides [2]. Since the polysulfides undergo disproportionation at a temperature of  $140^\circ$  [3], the cited analytical data, obviously, characterize the average composition of polysulfides with a variable number of sulfur atoms in the polysulfide bridge.

The formation of hydrogen sulfide was not observed on heating sulfur and Captax in sealed ampoules at  $140^\circ$ . From this it follows that the equilibrium of the reaction, in conformity with the equation:

\* The spectra were taken by R. P. Evstigneeva, for which the authors express their appreciation to her.



is characterized by an insignificant concentration of  $H_2S$ , and appreciable liberation of hydrogen sulfide occurs only under the above-cited conditions of its continuous elimination from the sphere of the reaction.

In sealed ampoules, the reaction between sulfur and MBT in the melt leads : a) to an exchange of sulfur in the mercapto group [4]; b) to the formation of a polysulfide containing more than 42.9% sulfur\*. This polysulfide was extracted from the cold reaction mixture with an aqueous solution of NaOH, which indicates the presence in the polysulfide of a mercapto group. The spectrum of this substance contained a maximum in the region of  $330 \text{ m}\mu$ ; however, it was not very clearly expressed (see Figure 4).

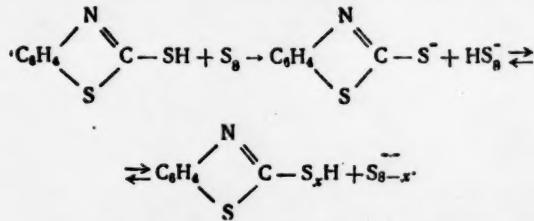
An analogous substance was extracted from a mixture of natural rubber, sulfur, and MBT after vulcanization in a press. The sulfur content of this polysulfide was more than 50.2%; the maximum in the region of  $330 \text{ m}\mu$  was rather clearly expressed.

Thus, the intermediate compound formed by the reaction of sulfur and MBT under vulcanization conditions is a polysulfide of the composition



The experimental data permit certain considerations on the mechanism of the action of MBT as a vulcanization accelerator. Fisher and a series of other investigators [6] have advanced the hypothesis that the vulcanization reaction is the formation of  $H_2S$  (as a result of the reaction of sulfur with rubber or accelerator) which then adds to the rubber with the formation of mercapto groups which are subsequently oxidized into disulfide or polysulfide "bridges" between molecular chains of rubber. Along with this, Fisher assumes a chain mechanism for this reaction. Our results are in contradiction with this hypothesis. As seen from the above-cited kinetic equation, the activation energy for the formation of  $H_2S$  by the reaction of sulfur and MBT is 33,500 cal/mole, which approximates the activation energy for the vulcanization process without an accelerator ( $U = 35,500 \text{ cal/mole}$ ) and considerably exceeds the apparent activation energy for vulcanization in the presence of MBT ( $U = 20,900 \text{ cal/mole}$ ). Such a high activation energy means an extremely slow process, and, therefore, the formation of  $H_2S$  cannot be considered as basic to vulcanization.

The following scheme for the reaction of sulfur with MBT under vulcanization conditions seems more probable to us :



\* The polysulfide was extracted with a solution of NaOH along with unchanged MBT; since the separation of these substances was not possible, the sulfur content presented above refers to the composition of the mixture. The sulfur content of the polysulfide itself is, obviously, substantially greater. The absence of free sulfur in the preparation was checked by the reaction of Garcia-Fernandez [5].

This scheme is confirmed by the discovery of a polysulfide of MBT in the reaction system.\* The vulcanization effect is basically determined by the reaction of rubber with sulfur biradicals,  $S_2^{--X}$  and with the radical

C6H4-C(=N)S-, the action of which under vulcanization conditions has been considered by us previously [8].

M. V. Lomonosov Moscow Institute of Fine Chemical Technology

Received November 3, 1955

#### LITERATURE CITED

- [1] F. Feher, Z. Angew. Chem., 67, 337 (1955); R. Bacon and R. Fanelli, J. Am. Chem. Soc., 65, 639 (1943).
- [2] H. P. Koch, J. Chem. Soc., 387 (1949).
- [3] G. Bloomfield, J. Chem. Soc., 1549 (1947).
- [4] G. A. Blokh, E. A. Golubkova and G. P. Mikhlin, Proc. Acad. Sci. USSR, 90, 201 (1953); E. N. Guryanova, Proc. Acad. Sci. USSR, 98, 229 (1954).
- [5] H. Garcia - Fernandez, Bull. soc. chim. (France), 594 (1947).
- [6] H. Fisher, Ind. Eng. Chem., 31, 1381 (1939); I. T. Tarenenko, Light Ind., 3, 24 (1955).
- [7] C. W. Bedford and L. B. Sebrell, Ind. Eng. Chem., 14, 25 (1922).
- [8] B. Dogadkin and V. Selyukova, Colloid J., 17, 215 (1955) (T. p. 199);\*\* Proc. Acad. Sci. USSR, 92, 61 (1953).

\* The formation of polysulfide as an intermediate product during the reaction of MBT with sulfur was assumed in a previous work [7].

\*\* (T. p. = C. B. Translation pagination)

## A THERMALLY STABLE VARIETY OF ALUMINUM HYDROXIDE

I. V. Krotov

(Presented by Academician G. G. Urazov, October 17, 1955)

A detailed study of the various hydrates of alumina was carried out fairly recently by N. S. Kurnakov and G. G. Urazov [1]. The authors showed that on the heating curve of crystalline synthetic alumina hydrate there is a break corresponding to the dihydrate form of alumina, which is found in nature as the trihydrate — hydrargillite — and as the monohydrate, diaspore.

In Mellor's reference work [2], it is indicated that three hydrates of aluminum oxide exist: diaspore,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; bauxite,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ; and Gibbsite,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . The existence of bauxite is disputed by some authors. Under natural conditions, the compound  $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  has been observed in crevices in dolomite. Some authors recognize the existence of a hexahydrate,  $\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ .

Z. Ya. Berestneva, T. A. Koretskaya and V. A. Kargin [3] established that aluminum hydroxide freshly prepared from aqueous solutions of aluminum chloride and ammonia at room temperature have an amorphous structure; on aging, the aluminum hydroxide finally acquires the structure of hydrargillite crystals (gibbsite).

Imelik, Mathieu, Prettre and Teicher [4] noted that aluminum hydroxide precipitated from an acid medium is amorphous, and that precipitated from an alkaline medium is crystalline.

The general question of the forms, the conditions of formation, and the existence of aluminum hydroxides is not simple; this question is partly complicated by the absence of a universal nomenclature for the various forms of aluminum hydroxide.

In the recently published works of de Boer, Fortuin and Steggerda [5,6] are given all the existing names for aluminum hydroxide, the mechanism of their dehydration is considered in detail, and the newest literature relating to the hydrate forms of aluminum oxide is cited. According to the data of de Boer, Fortuin and Steggerda, only practically anhydrous aluminum oxide occurs at temperatures above 500°.

The hydrated aluminum oxide which we studied was prepared at room temperature by the addition of a small excess of an aqueous solution of ammonia to an aqueous solution of aluminum sulfate. In this case, according to the literature data [6], bayerite is formed. The precipitate of aluminum hydroxide was washed with distilled water by decantation to the disappearance of the reaction for sulfate ion. One portion (A) of the thus prepared aluminum hydroxide was first dried in air at room temperature and then for 1 year in a desiccator over calcium chloride. The thus prepared preparation had a crystalline structure, and its grains differed very greatly in hardness, as was observed during grinding of the preparation in a mortar.

Another portion (B) of the aluminum hydroxide was dried in air at 60° and then stored for 1 year in a desiccator over calcium chloride. The thus obtained preparation did not have a crystalline structure, and easily crumbled to a powder on rubbing between the fingers.

We took thermograms of both samples of the preparation [7], using usually a sample size of about 6 g and a heating rate of about 10°/minute. With this sample size and heating rate, an irregularity in the course of the dehydration process was observed, as a rule, in the temperature interval 80-150°. With a smaller sample size and the same heating rate in the temperature interval 80-250°, the irregularity in the course of the dehydration process was absent.

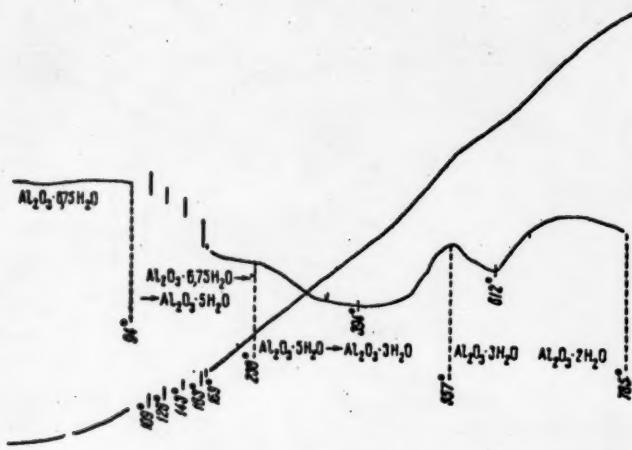


Fig. 1. Aluminum hydroxide Sample A (dried at room temperature and stored for 1 year in a desiccator).

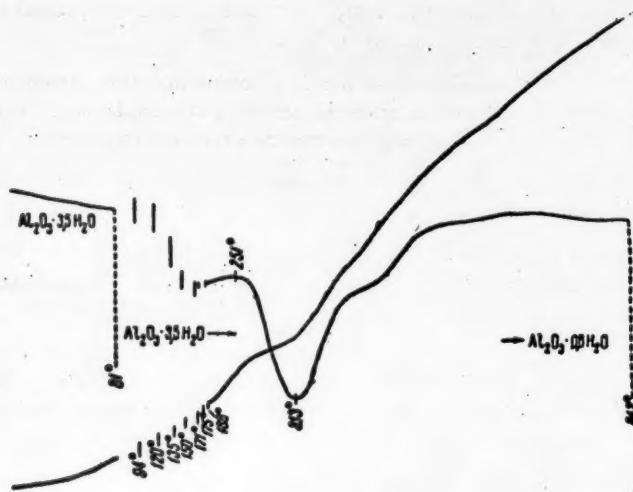


Fig. 2. Aluminum hydroxide Sample B (dried at 60° and stored for 1 year in a desiccator).

The total water content in the aluminum hydroxide sample was determined by the loss in weight of the sample after calcination at 1200° to constant weight.

In Figures 1 and 2 are presented curves of the direct and differential temperature records for hydrated aluminum oxide Samples A and B.

Water content determination for a sample heated to a given temperature was carried out by taking a special thermogram to the given temperature and determining the water content of the sample.

We did not carry out special experiments in which samples of aluminum hydroxide are maintained continuously for many hours at specific temperatures, the purpose of which would be to determine the equilibrium com-

position of the dehydration products; this is planned for the future.

As seen from Figures 1 and 2, the processes of the dehydration of aluminum hydroxide Samples A and B were very different. Samples A and B differed greatly from one another in initial water content (6.75 and 3.5 H<sub>2</sub>O per Al<sub>2</sub>O<sub>3</sub>, respectively), in composition of intermediate dehydration products, and in composition of final dehydration products after heating to approximately 800° (2 and 0.6 H<sub>2</sub>O per Al<sub>2</sub>O<sub>3</sub>, respectively).

In Figure 1 are shown the limits of existence of the various dehydration products of aluminum hydroxide Sample A at the conditions of thermographing.

Aluminum hydroxide Sample A displayed unusual thermal stability which, obviously, was dependent on an extra stable bond of the water with the aluminum oxide in this variety of aluminum hydroxide.

Institute of Physical Chemistry Academy of Sciences  
of the USSR

Received October 15, 1955

#### LITERATURE CITED

- [1] N. S. Kurnakov and G. G. Urazov, *J. Appl. Chem.*, 1, 13 (1924).
- [2] J. V. Mellor, *A Comprehensive Treatise of Inorganic and Theoretical Chemistry*, 5, 1946 p. 273-288.
- [3] Z. Ya. Berestneva, T. A. Koretskaya and V. A. Kargin, *Colloid J.*, 13, No. 5, 323 (1951).
- [4] B. Imelik, M. V. Mathieu, M. Prettre and S. Teicher, *J. Chem. Phys.*, 51, No. 11-12, 651 (1954).
- [5] J. H. de Boer, J. M. H. Fortuin and J. J. Steggerda, *Proc. Koninkl. Nederland Akad. Wetenschap.*, 57, No. 2, Ser. B, *Phys. Sci.*, 170 (1954).
- [6] J. H. de Boer, J. M. H. Fortuin and J. J. Steggerda, *Proc. Koninkl. Nederland Akad. Wetenschap.*, 57 No. 4, Ser. B, *Phys. Sci.*, 434 (1954).
- [7] L. G. Berg, A. V. Nikolaev and F. Ya. Rode, *Thermography*, Acad. Sci. USSR Press, 1944.



RELATIVE REACTIVITY OF THE C-Cl BONDS OF  $\alpha$ -AND  $\gamma$ -CHLORO-ALKYLTRIMETHYLSILANES IN THE REACTION WITH POTASSIUM IODIDE

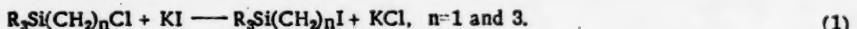
V. F. Mironov

(Presented by Academician B. A. Kazansky, November 5, 1955)

The widespread idea [1] that a halogen in organosilicon compounds which is attached to the  $\gamma$ -carbon relative to the Si atom is more reactive than one in the  $\alpha$ -position is based on the work of Sommer et al [2]. These authors studied the reaction of  $\alpha$ -and  $\gamma$ -chloroalkyltrichlorosilanes with alcoholic alkali, and came to the conclusion that a C-Cl bond in the  $\gamma$ -position to the Si is much more active than in the  $\alpha$ -position.

The effect of the R radicals in  $R_3SiCH_2X$  compounds on the mobility of the halogen in ionic exchange reactions with NaI, KSCN, and  $KOOCCH_3$  has previously been reported [3,4]. In these works it was established that substitution of methyl radicals at the Si atom by ethyl in  $(CH_3)_2SiCH_2X$  sharply decreased the activity of the halogens in the stated reactions.

In the present work we attacked the problem of clarifying the effect of the location of the halogen relative to the Si atom on its reactivity in nucleophilic substitution reactions. As the most convenient reaction for the realization of this purpose, we chose the reaction of  $\alpha$ -chloromethyltrimethylsilane (V)  $\gamma$ -chloropropyltrimethylsilane (VI) with KI.



It was shown that, in Reaction 1, the formation of  $\gamma$ -iodopropyltrimethylsilane (XIII) required 3-5 times longer than the formation of  $\alpha$ -iodomethyltrimethylsilane (XVI).

With the aim of increasing the precision of the results obtained, experiments were undertaken in which the cited compounds, used in the amount of 0.3 mole, were boiled together in an acetone medium with 0.3 mole of KI; that is, the same conditions were strictly observed in carrying out the reaction with both (V) and (VI). As a result, it was shown that the initial (V) was totally absent from the reaction mixture, but almost all of (VI) was recovered from the reaction unchanged. Further, 0.21 mole of  $\alpha$ -iodomethyltrimethylsilane was isolated, while (XIII) was recovered to the extent of only  $\sim 0.03$  mole.

Considering that a similar result was also obtained with KSCN, it can be considered that in bimolecular nucleophilic substitution reactions ( $S_N2$ ), the halogen in  $\alpha$ -silicon chlorides is considerably more mobile than in  $\gamma$ -silicon chlorides. The contradiction of these results with those of Sommer [2] is explained, apparently, not so much by a different reaction mechanism for  $\alpha$ - and  $\gamma$ -silicon chlorides with alkali than with KI, as by different mechanisms for the reaction of alkali with  $\alpha$ - and with  $\gamma$ -chloroalkyltrichlorosilanes.

Actually, it has been shown that  $\alpha$ -silicon chlorides split off methyl chloride under the action of alkali [5], that is, the reaction proceeds only at the Si-C bond, but  $\gamma$ -silicon chlorides split out cyclopropane [2,6], that is, the reaction proceeds both at the C-Cl bond and at the Si-C bond. Consequently, alcoholic alkali cannot be a reagent for characterizing the reactivity of C-Cl bonds in different organosilicon compounds, especially in  $\alpha$ -silicon chlorides, since the hydroxyl ion, probably, first attacks the Si-C bond.

By means of reaction (1) a series of new  $\alpha$ - and  $\gamma$ -silicon chlorides was also prepared, using for this synthesis certain new  $\alpha$ - and  $\gamma$ -silicon chlorides (see Table 1). The preparation of these high boiling  $\alpha$ -silicon chlorides by a previously described method [7] met with difficulty owing to a profuse liberation of elemental iodine. The initial  $\alpha$ - and  $\gamma$ -chloroalkylsilane chlorides were prepared by chlorination of dimethyl-dichlorosilane and propyltrichlorosilane in a previously described apparatus [7]. During this work, the optimal temperatures for the synthesis from  $(CH_3)_2SiCl_2$  of both  $ClCH_2Si(CH_3)Cl_2$  and  $Cl_2CH_2SiCHCl_2$  were established.

TABLE I

*See below	Yield, %	B.p., °C	Pres- sure, mm. Hg	$\eta_D^a$	$d_4^a$	MR <sub>D</sub>			Found, %			Calculated, %				
						Calc.	Found	Calc.	H	C	Si	Hal	H	C	Si	Hal
(VII)	84	150.5	744	1.4319	0.8769	44.46	44.38	40.62	47.76	47.96	18.51	18.53	10.03	47.82	18.62	23.53
(VIII)	65.5	64	62.1	1.4483	0.8976	53.49	53.34	50.68	53.56	53.70	15.83	15.90	10.71	53.74	15.71	19.43
(IX)	58	69-70	1	1.4515	0.8897	62.71	61.27	51.66	55.91	55.95	13.81	17.27	17.22	58.07	13.56	17.14
(X)	74.7	227	767	1.4460	0.8845	62.72	62.74	51.27	58.92	58.95	13.39	13.28	16.80	17.15	11.21	58.07
(XI)	60.6	93.5	227	1.4530	1.5717	65.55	65.58	61.16	67.52	67.57	11.20	11.14	15.06	15.21	6.12	68.13
(XII)	25	222	733	1.4530	1.5717	62.90	61.15	61.16	57.92	57.91	13.73	13.49	17.51	17.56	11.21	58.02
(XIII)	32	189.5	750	1.4303	1.3443	52.44	62.67	62.67	52.40	52.40	23.63	25.99	11.19	11.55	52.78	52.41
(XIV)	70	227-228	746	1.4344	1.2742	61.78	61.86	7.01	7.08	7.02	46.60	46.63	6.24	6.24	29.24	52.41
(XV)	43	191-192	744	1.4326	1.2136	52.82	52.82	52.40	40.38	40.19	9.30	9.37	6.24	6.24	29.73	52.41

\*  $\alpha$ - and  $\gamma$ -Haloalkyltrialkylsilanes

Chlorination of  $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$  under these conditions [7] of dropwise liquid condensation leads to the preparation of  $\text{Cl}_2\text{CHSi}(\text{CH}_3)_3$  and  $(\text{CH}_3)_2\text{Si}(\text{CH}_2\text{Cl})_2$  in a ratio of 1:1.8. It is well known that chlorination of these same compounds [8] in a similar apparatus [9] but under strictly vapor phase conditions leads to a ratio of 1:1.3 of these substances.

## EXPERIMENTAL

### Chloromethylmethyl dichlorosilane

$\text{ClCH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$  (I). Dichloromethylmethyl dichlorosilane  $\text{Cl}_2\text{CHSi}(\text{CH}_3)\text{Cl}_2$  (II). A. In the flask of the previously described apparatus [7] was placed 210 g of dimethyl dichlorosilane. Chlorination was carried out over a period of 25 hours, during which the temperature of the liquid in the flask did not reach 126°. By distillation in a column, there was obtained 3 g of the initial  $(\text{CH}_3)_2\text{SiCl}_2$ , 203 g (I), b. p. 120-121°, yield 76.5%, and 53 g of (II), b. p. 148-149°, yield 16.5%. 12 g of higher chlorides was in the residue.

B. Chlorination, under the same conditions, of 500 g of  $(\text{CH}_3)_2\text{SiCl}_2$  at a temperature of about 149° gave: (I) - 75 g, yield 11.8%; (II) - 430 g, yield 56%; and 103 g of a fraction boiling at 155-165° (a mixture of trichlorides).

### Bis-(chloromethyl)-dimethylsilane

$(\text{ClCH}_2)_2\text{Si}(\text{CH}_3)_2$  (III). Dichloromethyl trimethylsilane  $\text{Cl}_2\text{CHSi}(\text{CH}_3)_3$  (IV). By the chlorination of 154 g of chloromethyl trimethylsilane (V) under the described conditions and at about 135°, which required 20 hours, there was obtained: initial (V) 33.5 g, b. p. 97-98°; 48.7 g of (IV), b. p. 131-132°; and 87.4 g (III), b. p. 153°. The total yield of dichlorides (III) and (IV) was 88% of the (V) entering into the reaction. The ratio of the amounts of (III) and (IV) was 1:1.8.

$\alpha$ -Chloromethyl trimethylsilane  $\text{ClCH}_2\text{Si}(\text{CH}_3)_3$  (V).  $\text{CH}_3\text{MgCl}$  was prepared from 73 g Mg in 1.3 liters of ether in a 2-liter flask. Methylchloride was passed into the mixture for a period of 10 hours until all of the Mg disappeared. The addition of 190 g of (I) was carried out while cooling the flask with water. After the addition of ~ 1/3 of the (I), the contents of the flask solidified; the remaining quantity of (I) was carefully poured into the flask, and it was allowed to stand overnight. The contents of the flask were then boiled for 6 hours, and were decomposed with water containing HCl. The ether layer was added to the ethereal extract of the water layer, and was dried over  $\text{CaCl}_2$ . After distilling off the ether, distillation of the remaining liquid in a column gave 128 g (V), b. p. 97-98°, yield 90%. The average yield of 6 syntheses carried out on the same scale was 85%.

$\gamma$ -Chloropropyltrimethylsilane  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  (VI). To  $\text{CH}_3\text{MgI}$  (prepared from 30 g of Mg and 200 g of  $\text{CH}_3\text{I}$  in 0.5 liter of ether) was added 62 g of  $\gamma$ -chloropropyltrichlorosilane [10]. On the following day, the contents of the flask were boiled for 5 hours, and, after the usual treatment described in the synthesis of (V), there was obtained 37 g of (VI), b. p. 150-153°, yield 84%.

$\gamma$ -Chloropropyldiethylmethylsilane  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{CH}_3$  (VII). To  $\text{C}_2\text{H}_5\text{MgBr}$  (prepared in 0.9 liter of ether from 49 g of Mg and 250 g of  $\text{C}_2\text{H}_5\text{Br}$ ) was added, with cooling, 192 g of  $\gamma$ -chloropropylmethyl dichlorosilane over a period of 1.5 hours. On the following day, after 6 hours boiling and the usual treatment, there was obtained 117.4 g of (VII), b. p. 63-66° (3 mm), yield 65.6%.

$\gamma$ -Chloropropyldipropylmethylsilane  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{n-C}_3\text{H}_7)_2\text{CH}_3$  (VIII). To  $\text{n-C}_3\text{H}_7\text{MgBr}$  (prepared in 0.5 liter of ether from 24 g Mg and 150 g of  $\text{n-C}_3\text{H}_7\text{Br}$ ) was added 96 g of  $\gamma$ -chloropropylmethyl dichlorosilane. After 7 hours boiling and the usual treatment, there was obtained 60 g of (VIII), b. p. 66-70° (~1mm), yield 58%.

$\alpha$ -Chloromethyldibutylmethylsilane  $\text{ClCH}_2\text{Si}(\text{n-C}_4\text{H}_9)_2\text{CH}_3$  (IX). To  $\text{n-C}_4\text{H}_9\text{MgBr}$  (prepared in 1 liter of ether from 50 g of Mg and 150 g of  $\text{n-C}_4\text{H}_9\text{Br}$ ) was added 140 g of (I). On the following day, boiling was continued for 9 hours. Then, after the usual treatment [see synthesis of (V)], there was obtained 132 g of (IX), b. p. 227-228°, yield 74.7%.

$\alpha$ -Chloromethyldiphenylmethylsilane  $\text{ClCH}_2\text{Si}(\text{C}_6\text{H}_5)_2\text{CH}_3$  (X). 57.6 g of (I) was added to  $\text{C}_6\text{H}_5\text{MgBr}$ , prepared from 24.3 g of Mg and 160 g of  $\text{C}_6\text{H}_5\text{Br}$  in 0.5 liter of ether. After 5 hours boiling, there was obtained 60.6 g of (X), b. p. 91-94°, yield 60.6%.

$\alpha$ -Chloromethyltripropylsilane  $\text{ClCH}_2\text{Si}(\text{n-C}_3\text{H}_7)_3$  (XI). To  $\text{n-C}_3\text{H}_7\text{MgBr}$ , prepared in 0.5 liter of ether from 36 g of Mg, was added 82 g of chloromethyltrichlorosilane [4]. After 7 hours boiling and the usual treatment, and after repeated distillations in a column, there was obtained 23 g of (XI), b. p. 222-223°, yield 25%.

$\alpha$ -Iodomethyldipropylmethylsilane  $\text{ICH}_2\text{Si}(\text{n-C}_3\text{H}_7)_2\text{CH}_3$  (XII). In a 1-liter flask with reflux condenser was placed 38 g of  $\alpha$ -chloromethyldipropylmethylsilane [10], 50 g of KI, and 0.5 liter of acetone. The contents of the flask were boiled for 45 hours with 5 overnight interruptions. The salt was then filtered off, the acetone was distilled from the filtrate, and the liquid remaining on the previously filtered salt was washed off with water. After drying over  $\text{CaCl}_2$ , distillation yielded 41 g of (XII), b. p. 225-230°, yield 71.5%.

$\gamma$ -Iodopropyltrimethylsilane  $\text{ICH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$  (XIII). A mixture of 0.5 liter of acetone, 35 g of (VI), and 50 g KI was boiled for 32 hours in a 1-liter flask. After the treatment described in the synthesis of (XII), 32 g of unchanged (VI) was recovered. A second boiling of the recovered 32 g of (VI) with 40 g of KI in 0.4 liter of acetone was carried out over 13 9-hour days. After the usual treatment, there was obtained 22 g of (XIII), b. p. 187-193°, yield 43%. In repeated distillations the b. p. was 191-192°.

There were synthesized, under analogous conditions, the  $\alpha$ -silicon iodides (XIV) - boiling time 26 hours, and (XV) - boiling time 70 hours.  $\alpha$ -Iodomethyltrimethylsilane (XVI) [11] was prepared in 75% yield from (V) with 32 hours boiling.

Synthesis of (XIII) and (XVI) under the same conditions. In a 2-liter flask fitted with a reflux condenser were placed 36.8 g of (V), 45 g of (VI), 50 g of KI, and 1.1 liters of acetone which had been dried over  $\text{CaCl}_2$  and distilled with  $\text{KMnO}_4$ . The contents of the flask were boiled for 32 hours with 3 overnight interruptions. The precipitated salt was then filtered and dissolved in 200 ml of water, and this solution was later used to wash the residue from the distillation of acetone from the filtrate. The organic layer was separated, dried over  $\text{CaCl}_2$ , and distilled in a column of 20 theoretical plates. We were not successful in recovering the initial (V). The mixture was distilled into the following fractions: 138-150°, 86 g; 150-180°, 3 g; and 180-190°, 8 g. A second distillation of the 138-150° fraction gave 45 g of (XVI) (b. p. 139-139.5°,  $n_D^{20}$  1.4915, yield 70%) and 38 g of initial (VI) (b. p. 149-150°,  $n_D^{20}$  1.4332). By a second distillation of the 180-190° fraction, there was isolated about 7 g of (XIII), b. p. 185-190°,  $n_D^{20}$  1.4885, yield ~ 9%.

#### LITERATURE CITED

- [1] A. Ya. Yakubovich and V. A. Ginzburg, *Prog. Chem.*, 18, No. 1, 62 (1949); K. A. Andrianov and A. A. Zhdanov, *Prog. Chem.*, 21, No. 2, 201 (1952); H. Gilman, G. E. Dunn, *Chem. Rev.*, 52, 109 (1953).
- [2] L. H. Sommer, E. Dorfman, et al., *J. Am. Chem. Soc.*, 68, 488 (1946).
- [3] V. B. Miller, M. B. Neiman et al., *Proc. Acad. Sci. USSR*, 101, No. 3, 495 (1955).
- [4] A. D. Petrov, V. F. Mironov and N. A. Pogonkina, *Proc. Acad. Sci. USSR*, 100, No. 1, 81 (1955).
- [5] R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, 67, 1810 (1945).
- [6] L. H. Sommer, R. E. Van Strien and F. C. Whitmore, *J. Am. Chem. Soc.*, 71, 3056 (1949).
- [7] V. A. Ponomarenko and V. F. Mironov, *Proc. Acad. Sci. USSR*, 94, No. 3, 485 (1954).
- [8] J. D. Roberts, S. Dev, *J. Am. Chem. Soc.*, 73, 1879 (1951).
- [9] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509 (1951).
- [10] V. F. Mironov and N. A. Pogonkina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, No. 1, 182 (1955). (T. p. 161)\*
- [11] F. C. Whitmore, L. H. Sommer, *J. Am. Chem. Soc.*, 68, 481 (1946).

\*(T. p. = C. B. Translation pagination)

## ACIDITY FUNCTION OF THE SYSTEM $H_2SO_4 - HSO_3Cl$

V. A. Palm

(Presented by Academician V. N. Kondratyev, October 22, 1955)

The acidity function  $H_0$ , introduced by Hammet, is an important physicochemical characteristic of strong acid media. The concept of acidity function is especially fruitful in its application to the quantitative aspects of acid catalysis in concentrated acids where the concept of pH loses its significance.

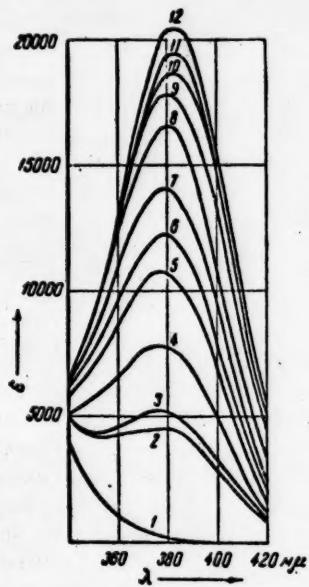


Fig. 1. Absorption spectra of p-nitrochlorobenzene: 1) in 95%  $H_2SO_4$ ; 2) in 100%  $H_2SO_4$ ; 3-12) in mixtures of  $H_2SO_4$  and  $HSO_3Cl$  of  $HSO_3Cl$  contents of 4.1; 11.1; 24.8; 37.9; 54.6; 69.8; 81.0; 88.2; 97.5; and 100 mole %, respectively

the use of spectrophotometric determination of the degree of ionization of certain aromatic nitro compounds as an accurate method for the determination of the concentration of sulfuric acid in the region near 100%  $H_2SO_4$ .

We prepared the mixtures of  $H_2SO_4$  and  $HSO_3Cl$  by mixing 100%  $H_2SO_4$  with pure, distilled  $HSO_3Cl$ . 100%  $H_2SO_4$  was prepared by the method of Brand with an error in the content of  $H_2SO_4$  not exceeding 0.02%.

p-Nitrochlorobenzene, 2,4-dinitrotoluene, and p-nitrotoluene were used as indicators. Brand gave for these indicators the following values of  $pK_a$ : p-nitrotoluene - 10.34 [3]; p-nitrochlorobenzene - 11.49 [3] and

As is well known,  $H_0$  is related to the degree of ionization of a base in the given medium by the equation

$$H_0 = pK_a + \log \frac{[B]}{[BH^+]},$$

where  $K_a$  is the dissociation constant of the acid  $BH^+$  in water, which is conjugate with the base B.

The problem of studying the acidity function of the system  $H_2SO_4 - HSO_3Cl$  was set before us. As is well known, chlorosulfonic acid is used as a reagent in various organic syntheses. It attained special significance in industry in connection with the so-called chlorosulfonation reaction. It is quite probable that both this and other reactions taking place in mixtures of  $H_2SO_4$  and  $HSO_3Cl$  are of the acid-catalyzed type. If this is so, then a study of the acidity function of the system  $H_2SO_4 - HSO_3Cl$  is prerequisite to a more detailed study of the mechanism and kinetics of these reactions.

The acidity function of the system  $H_2O - SO_3$  has been studied by several authors [1-5]. Particular attention is directed to the work of Brand [3,4], in which is described the use of aromatic nitro compounds as indicators for the determination of  $H_0$  in highly acid media. He also developed a very precise method for the determination of the  $SO_3$  content of oleum by titration with water [6]. The cited work also permits

-11.56 [4]; 2,4-dinitrotoluene -12.6 [4]. In the calculation of these values of  $pK_a$ ,  $H_0$  for 100%  $H_2SO_4$  was taken as -10.89. Other sources give the figure -19.60 [2,5]. Since the absolute value of the acidity function of  $H_2SO_4$ , which was used as the initial point of the reading, does not effect the relative values of  $H_0$  in the system  $H_2SO_4$ - $HSO_3Cl$  with an increase in the concentration of  $HSO_3Cl$ , this question will not be discussed here. The first of the above-mentioned values was used as a base in the present work.

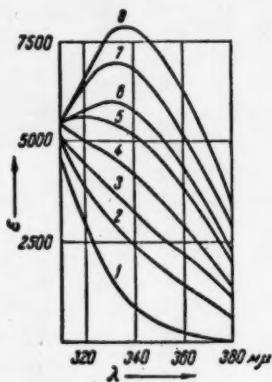


Fig. 2. Absorption spectra of 2,4-dinitrotoluene: 1) in 95%  $H_2SO_4$ ; 2-8) in mixtures of  $H_2SO_4$  and  $HSO_3Cl$  of  $HSO_3Cl$  contents of 54.5; 69.8; 81.0; 88.2; 95.0; and 100 mole%, respectively.

vestigated. The same thing can also be said for 2,4-dinitrotoluene in the 100%  $H_2SO_4$ , prepared by us, at a wave length of  $\lambda = 365 m\mu$  was 15,400, which agrees well with the data of Brand [3]. The same can also be said for p-nitrochlorobenzene, the value for which was 4,260.

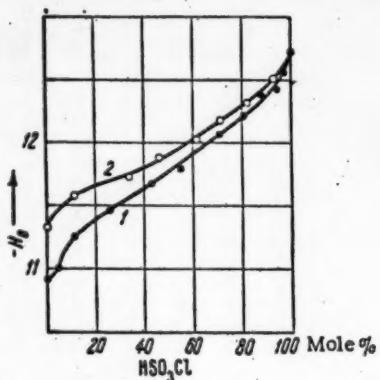


Fig. 3

of 2,4-dinitrotoluene given by Brand is  $\epsilon_{335m\mu}^{ion} = 13900$  [4]. The absorption coefficient of the un-ionized form is  $\epsilon_{335m\mu} = 1700$ . Depending on the acidity of the medium, maximum absorption lies in the region of 330 to 335  $m\mu$ .

The results of the determinations of the acidity function with p-nitrochlorobenzene are presented in Table 1.

The values of  $pK_a$  for 2,4-dinitrotoluene were made somewhat more precisely by us, as may be seen from the data of Table 2. The value obtained for  $pK_a$ , -12.74, was used for the calculation of  $H_0$  in media with high  $HSO_3Cl$  contents where the data obtained with p-nitrochlorobenzene became inaccurate. The results obtained are presented in Table 3.

Experimental method. Solutions of the indicators, purified by recrystallization, were prepared in 100%  $H_2SO_4$  with accurately known concentrations of the order of 0.01 mole/kg. A batch of such a solution of the order of 20 mg was taken in a piece of capillary tube and placed in a dismountable cell with quartz windows. Filling of the cell with the mixture of  $H_2SO_4$  and  $HSO_3Cl$  was carried out through a tube connected by means of a ground joint. The quantity of acid mixture added was weighed (about 5 g). Cells with thicknesses of 0.790 and 0.540 cm were used. Absorption spectra of the indicators relative to the solvent were measured with a SF-4 spectrophotometer.

Since p-nitrotoluene is easily sulfonated in 100%  $H_2SO_4$  and still more easily in mixtures of  $HSO_3Cl$ , we used this indicator only for checking the 100%  $H_2SO_4$ . p-Nitrochlorobenzene is practically completely stable in 100%  $H_2SO_4$ . In the time required for measuring the spectra of this indicator, it did not undergo a change in any of the mixtures investigated. The absorption coefficient of p-nitrotoluene in the 100%  $H_2SO_4$ , prepared by us, at a wave length of  $\lambda = 365 m\mu$  was 15,400, which agrees well with the data of Brand [3]. The same can also be said for p-nitrochlorobenzene, the value for which was 4,260.

Absorption spectra of p-nitrochlorobenzene in various mixtures of  $H_2SO_4$  and  $HSO_3Cl$  are presented in Figure 1, and the spectra of 2,4-dinitrotoluene are presented in Figure 2.

The values of  $H_0$  from p-nitrochlorobenzene were calculated using the measured values of the absorption coefficient,  $\epsilon$ ; at maximum absorption of the ionized form in the wave-length interval  $\lambda = 375$  to  $382 m\mu$ . Brand, working at a wave length of  $\lambda = 365 m\mu$ , did not arrive at a value for the absorption coefficient of the completely ionized indicator at maximum absorption. This value, calculated from a comparison of the experimental data of Brand [3] with our data, is  $\epsilon_{382m\mu}^{ion}$ . The absorption coefficient of the un-ionized form is  $\epsilon_{380m\mu}^0 = 200$ .

The absorption coefficient of the ionized form of 2,4-dinitrotoluene given by Brand is  $\epsilon_{335m\mu}^{ion} = 13900$  [4]. The absorption coefficient of the un-ionized form is  $\epsilon_{335m\mu} = 1700$ . Depending on the acidity of the medium, maximum absorption lies in the region of 330 to 335  $m\mu$ .

TABLE 1

HSO <sub>3</sub> Cl conc., in mole %	$\epsilon_{375-378 \text{ m}\mu}$	$H_0$	HSO <sub>3</sub> Cl conc., in mole %	$\epsilon_{375-378 \text{ m}\mu}$	$H_0$
0	4400	-10.89	69.8	16150	-12.06
4.1	5200	-10.98	81.0	17850	-12.21
11.1	7650	-11.25	88.2	18750	-12.37
24.8	10900	-11.48	95.0	19000	-12.42
37.9	12100	-11.61	97.5	19500	-12.55
54.6	14050	-11.78	100	20400	-

TABLE 2

HSO <sub>3</sub> Cl conc., in mole %	$\epsilon_{330 \text{ m}\mu}$	$H_0$	pK <sub>a</sub>
54.6	3100	-11.78	-12.70
69.8	3800	-12.06	-12.78
81.0	4700	-12.21	-12.74
88.2	5600	-12.37	-12.74

Average -12.74

TABLE 3

HSO <sub>3</sub> Cl conc., in mole %	$\epsilon_{330 \text{ m}\mu}$	$H_0$
95.0	6000	-12.43
97.5	7000	-12.56
100	7900	-12.78

The form of the curve relating  $H_0$  to HSO<sub>3</sub>Cl concentration (Figure 3, Curve 1) shows that the H<sub>2</sub>SO<sub>4</sub> does not simply "dilute" the chlorosulfonic acid, but enters into a chemical reaction with it as a base with an acid. Otherwise, the addition of a small amount of H<sub>2</sub>SO<sub>4</sub> to HSO<sub>3</sub>Cl would not exhibit the substantial effect on the value of  $H_0$ , and the addition of a small amount of HSO<sub>3</sub>Cl to H<sub>2</sub>SO<sub>4</sub> would lead to a somewhat sharper increase in the acidity of the medium.

The difference of 1.89 units in the absolute values of  $H_0$  between 100% HSO<sub>3</sub>Cl and 100% H<sub>2</sub>SO<sub>4</sub> shows that the first acid is 70 times stronger than the second. In all the systems for which  $H_0$  was measured, the mixture of H<sub>2</sub>SO<sub>4</sub> and HSO<sub>3</sub>Cl was comparable in acidity only to oleum.

From the above, we must expect chlorosulfonic acid to be one of the strongest acid catalysts.

We also carried out a measurement of  $H_0$  in media prepared by mixing chlorosulfonic acid with oleum having a free SO<sub>3</sub> content of 0.5% (Figure 3, Curve 2).

I express my deep appreciation to my scientific leader N. M. Chirkov for presenting the problem of the measurement of the acidity function of the system H<sub>2</sub>SO<sub>4</sub>—HSO<sub>3</sub>Cl in connection with a study of the mechanism of the process of chlorosulfonation and for advice in the course of the work.

Tartu State University

Received October 19, 1955

#### LITERATURE CITED

- [1] L. P. Hammet and M. A. Paul, *J. Am. Chem. Soc.*, 56, 830 (1934).
- [2] R. J. Gillespie and D. J. Millen, *Quart. Rev.*, 2, 277 (1948).
- [3] J. C. D. Brand, *J. Chem. Soc.*, (1950), 997.
- [4] J. C. D. Brand, *J. Chem. Soc.*, (1952), 1374.
- [5] Ch. D. Corgell, *J. Inorganic and Nuclear Chemistry*, March, 119 (1955).
- [6] J. C. D. Brand, *J. Chem. Soc.*, (1946), 585.

## SYNTHESIS AND PROPERTIES OF POLYHYDRIC PHENOLS

P. I. Sanin and A. V. Ulyanova

(Presented by Academician A. V. Topchiev, September 25, 1955)

We have shown that individual representatives of ethers of polyhydric phenols are surface-active substances, depressors which can lower the temperature of "congealing" [pour point] of paraffinic oils. It was of interest to establish the dependence between the activity of different ethers as depressors and their chemical structure.

There have been described in the literature the preparation and properties of certain mono- and diethers of dihydric phenols - pyrocatechol, resorcinol, and hydroquinone - and of the trihydric phenol phloroglucinol [1, 2]. Among the ethers described are ethers of relatively low molecular weight, the alkyl radicals of the ether groups containing not more than 5 carbon atoms; in addition, phenyl and benzyl ethers of these phenols are described. In the patent literature [3] are given instructions for the preparation of certain high molecular ethers of polyhydric phenols, but these instructions are extremely limited and the properties given are far from complete.

We have synthesized a series of ethers of polyhydric phenols, not described in the literature, having various numbers of alkoxy groups occupying different positions in the benzene nucleus; the alkyl radicals of the alkoxy groups were of different size and different structure, normal and branched. The properties, analytical results, and test results of the synthesized ethers are presented in Table 1.

The phenol ethers were prepared by heating the phenol, an alkyl halide (in the majority of cases, the bromide), and potassium hydroxide, taken in equimolar ratio, in alcoholic solution; in some experiments, the alkyl halide was used in larger amount.

The ethers prepared (with the exception of the octadecyl ethers, which were soluble only at elevated temperatures) were readily soluble in benzene, acetone, and chloroform at ordinary temperatures and in ethyl alcohol with heating; the monoethers of resorcinol were readily soluble in ethyl alcohol in the cold. The high molecular ethers of dihydric phenols were insoluble in water and did not dissolve in alcoholic potassium hydroxide with the formation of phenolates. It was established that some high molecular ethers of phenols partially rearranged during vacuum distillation - alkyl phenols were formed from the phenol ether. As is well known, some ethers of monohydric phenols undergo an analogous transformation on heating with hydrochloric acid [4, 5] or under the effect of aluminum chloride [6].

The majority of the ethers were prepared with yields comprising 40-75% of the theoretical yield. The yields of high molecular (octadecyl) ethers were lower.

The following conclusions can be made from the results of the tests of the ethers presented in Table 1.

1. The effect of the ethers as pour point depressors increased according to the extent of the increase in the number of aliphatic radicals connected with ether oxygens (Preparations Nos. 1, 3, and 11), the monoethers of phenols being completely inactive (Nos. 1 and 2).
2. The depressor effect of the di-n-octyl ethers of different phenols, in other words, ethers of resorcinol (No. 3), pyrocatechol (No. 9), and hydroquinone (No. 10), which contain alkoxy groups in the meta, ortho, and para positions, differed. The ether containing alkoxy groups in the meta positions was the most active.
3. The activity as depressors of the resorcinol diethers increased with an increase in the length of the aliphatic radical of normal structure attached to the oxygen of the ether group (Nos. 3 and 6). However, this occurred only up to a certain limit, since, with a considerable increase in the length of the aliphatic radicals, the oil solubility of the ether decreased to such an extent that the ether itself took part in the formation of structure (No. 8).

TABLE I. Ethers of Polyhydric Phenols

Preparation No.	Formula	Structure	$\eta_D^{25}$	M. p., °C	B. p., °C	Mol. wt.	Analysis			Pour Point Depressed, °C			
							calculated	found	%	C	H	C	
1	$C_{10}H_{12}O_2$		1.0194	517.5	164-167 (3 mm)	—	222.1; 220.3	222.3	75.63; 75.56	9.92; 10.04	75.63	9.96*	0
2	$C_{10}H_{12}O_2$		0.9725	1.5049	160-161 (2 mm)	—	216.2; 217.0	222.9	75.62; 75.60	9.68; 9.97	75.63	9.98**	0
3	$C_{10}H_{12}O_2$		0.8976	1.4770	162 (2 mm) ( $\eta_D^{25}$ )	37.5	329.2; 333.2	334.5	78.92; 79.03	11.37; 11.49	78.98	11.45	6
4	$C_{10}H_{12}O_2$		0.9168	1.4835	168-170 (2 mm)	—	331.6; 335.3	334.5	78.62; 78.82	11.43; 11.24	78.98	11.45	2
5	$C_{10}H_{12}O_2$		0.9010	1.4859	218-219 (2 mm)	—	386.2; 388.6	390.6	80.03; 79.98	11.90; 11.93	78.94	11.87	0
6	$C_{10}H_{12}O_2$		—	—	54.4-54.6	415.0; 417.7	419.7	80.35; 80.08	12.13; 12.14	80.32	12.04	8	
7	$C_{10}H_{12}O_2$		0.8973	1.4830	230-232 (1 mm)	—	—	—	80.87; 81.03	12.14; 12.34	80.04	12.32	9
8	$C_{10}H_{12}O_2$		—	—	80.0-80.5	608.4; 604.9	615.0	82.17; 82.01	12.82; 12.87	82.02	12.73	Pour point increased	
9	$C_{10}H_{12}O_2$		—	—	202-203 (4 mm)	24.0-24.5	338.4; 331.6	334.5	70.07; 70.00	11.70; 11.62	78.98	11.45	2
10	$C_{10}H_{12}O_2$		—	—	56.0-56.5	338.9; 330.8	334.5	78.92; 78.84	11.42; 11.48	78.98	11.45	1	
11	$C_{10}H_{12}O_2$		—	—	234-235 (1 mm)	—	438.6; 430.9	432.7	77.82; 77.87	11.90; 11.71	77.98	11.78	12
12	$C_{10}H_{12}O_2$		—	—	79.0-80.0	630.7; 636.0	631.0	80.02; 80.19	12.56; 12.48	78.94	12.48**	8	

\* In Preparation No. 1. Found, %: OH 8.03; 7.98. Calculated, %: OH 7.65. \*\* In Preparation No. 2. Found, %: OH 7.47; 7.77. Calculated, %: OH 7.65. \*\*\* In Preparation No. 12. Found, %: OH 2.77. Calculated, %: 2.69.

4. An increase in branching of the aliphatic radicals connected with the ether oxygen decreased the activity of the ethers as depressors (Nos. 3, 4 and 5). Ethers containing normal aliphatic radicals were the most effective.

## EXPERIMENTAL

Di-(dimethyloctyl) ether of resorcinol. From technical geraniol, a fraction was isolated which distilled from 115 to 120° at 8 mm pressure (the major portion distilled at 118°). The geraniol was separated from this fraction by converting it into the calcium chloride complex [7], and the oil obtained upon decomposition of the complex was then subjected to fractionation under vacuum. The pure geraniol, 2, 6-dimethyloctadiene-2, 6-ol-8, had a b. p. of 110-111° (9mm) [7]. Subsequent reduction of the geraniol into tetrahydrogeraniol was carried out over Raney nickel under hydrogen pressure [8]. The thus prepared tetrahydrogeraniol, 2, 6-dimethyloctanol-8, had a b. p. of 108.5-109° at 15 mm [9]. Tetrahydrogeranyl bromide was prepared from the tetrahydrogeraniol by the action of hydrogen bromide [8]. The properties of the bromide obtained, 8-bromo-2, 6-dimethyloctane (b. p. 109-110° at 18 mm) agreed with the literature data [8, 9]. From 2.4 g (0.022 mole) of resorcinol, 11.5 g (0.052 mole) of 8-bromo-2, 6-dimethyloctane, and 2.47 g (0.044 mole) of potassium hydroxide was obtained 4.0 g of a mixture of the mono- and diethers of resorcinol. From this mixture, by means of 5-fold distillation under vacuum, was isolated 2.0 g of pure di-(3, 7-dimethyloctyl) ether of resorcinol — a colorless, transparent, oily liquid having almost no odor. This ether was readily soluble in petroleum ether, benzene, acetone, and chloroform; it was difficultly soluble in alcohol on heating. B. p. 218-219° (2 mm).

Di-n-undecyl ether of butylresorcinol. Butylresorcinol, which had a m. p. of 68.0-69.5° in agreement with the literature data [10, 11], was prepared by the condensation of resorcinol with n-butyric acid in the presence of anhydrous zinc chloride [10]. The butylresorcinol was then reduced by Clemmensen reduction (amalgamated zinc and hydrochloric acid) [10-12]. The n-butylresorcinol obtained had a m. p. of 49-50°; the literature gives a m. p. of 47-48° [10], but according to earlier indications, butylresorcinol is an oily liquid [11]. 6.0 g (0.036 mole) of butylresorcinol, 20 g (0.085 mole) of n-undecylbromide, and 4.04 g (0.072 mole) of potassium hydroxide were used for the preparation of the ether. 11.9 g of a mixture of the mono-undecyl and diundecyl ethers of butylresorcinol was obtained from the reaction and subsequent purification. After multistage fractional distillation under vacuum, a fraction corresponding to the diether was additionally purified by treatment with silica gel and subsequent desorption of the diether with heptane. The yield was 2.6 g. The di-n-undecyl ether of butylresorcinol (1-butyl-2, 4-dihydroxybenzene) was a viscous, transparent, light yellow liquid. It was readily soluble in heptane, benzene, xylene, ether, and acetone, and difficultly soluble in alcohol. B. p. 230-232° (1 mm).

Di-n-octadecyl ether of resorcinol. n-Octadecyl alcohol was prepared by the reduction of ethyl stearate with hydrogen in the presence of the copper chromite catalyst,  $\text{Cr}_2\text{O}_3 \cdot 2\text{CuO}$ , of Adkins and Connor [13-15]. The reduction was carried out in a 500-cc rotating autoclave under preestablished optimum conditions: 100 g of ether charged; 5 g (5%) of  $\text{Cr}_2\text{O}_3 \cdot 2\text{CuO}$  catalyst; an experiment temperature of 260°; in initial hydrogen pressure of 150 atm.; maximum pressure was attained at the experiment temperature of 260°; duration of the experiment was 2 hours. The reaction products together with the catalyst were treated, with heating, with 500 cc of ethyl alcohol, and the catalyst was filtered from the alcoholic solution. After concentration of the alcoholic solution, the precipitated crystalline material was recrystallized from ethyl alcohol and distilled under vacuum. 75.4 g (87.2% of the theoretical yield) of pure, primary n-octadecyl alcohol, m. p. 58.5-59.0°, b. p. 168-174° (2 mm) [16-19], was obtained. Octadecyl bromide, which melted at 28.5-29.0°, literature value 28.5° [20], was prepared from the octadecyl alcohol. For the preparation of the di-n-octadecyl ether of resorcinol were used 1.2 g (0.011 mole) of resorcinol, 8.65 g (0.026 mole) of octadecyl bromide, and 1.24 g (0.022 mole) of potassium hydroxide. A preliminary experiment showed that the reaction proceeded very feebly when absolute ethyl alcohol was used as the solvent. In order to increase the reaction temperature, cyclohexanone was substituted for the alcohol; heating of the reaction mixture at the boiling point of cyclohexanone was carried out for 6 hours. The usual route was used for the separation of the mixture of ethers, from which, by multiple recrystallization from ethyl alcohol and also from a mixture of ethyl alcohol and petroleum ether, was obtained 0.8 g of the di-n-octadecyl ether of resorcinol—lustrous white crystals having a m. p. of 80-80.5°. The ether was soluble in chloroform, soluble with heating in petroleum ether, and difficultly soluble in benzene, acetone, and alcohol.

#### LITERATURE CITED

- [1] Beilstein, Handbook, 6, 759, 843, 1101 (1910).
- [2] E. Klarmann, L. W. Gatvas and V. A. Shternov, J. Am. Chem. Soc., 53, 3397 (1931).
- [3] J. H. Werntz, US Patent 2067960; Chem. Abstr., 31, 1428 (6) (1937).
- [4] N. I. Kursanov, J. Russ. Phys.-Chem. Soc., 46, No. 4, 838 (1914).
- [5] N. I. Kursanov, J. Russ. Phys.-Chem. Soc., 48, No. 5, 1172 (1916).
- [6] C. Thomas, Anhydrous Aluminum Chloride in Organic Chemistry, trans. from the English, Foreign Lit. Press, 1949, p. 706.
- [7] N. Ya. Demyanov, V. I. Nilov and V. V. Vilyams, Essential Oils, Their Composition and Analysis, Moscow-Leningrad, 1933, p. 87.
- [8] L. J. Smith, H. E. Ungnade, et al., J. Org. Chem., 4, No. 3, 334 (1939).
- [9] W. Longuinoff, E. Margoliss, Bull. soc. chim., 45, 156 (1929).
- [10] A. R. L. Dohme, E. H. Cox and E. Miller, J. Am. Chem. Soc., 48, 1688 (1926).
- [11] T. B. Johnson and F. W. Lane, J. Am. Chem. Soc., 43, 348 (1921).
- [12] Organic Reactions, Vol. I, trans. from the English, Foreign Lit. Press, 1948, p. 194.
- [13] H. Adkins and R. Connor, J. Am. Chem. Soc., 53, 1091 (1931).
- [14] K. Folkers and H. Adkins, J. Am. Chem. Soc., 54, 1145 (1932).
- [15] H. Adkins, Reactions of Hydrogen with Organic Compounds over Copper Chromium Oxide and Nickel Catalysts, Wisconsin, 1937, p. 97.
- [16] P. A. Levene, C. J. West and I. Scheer, J. Biol. Chem., 20, 524 (1915).
- [17] H. I. Backer and I. Strating, Rec. trav. chim. Pays-Bas, 59, 933 (1940).
- [18] F. Kraff, Ber., 16, 1723 (1883).
- [19] M. E. Andre and Th. Francois, Compt. rend., 183, 664 (1926).
- [20] A. Oskerko, J. Russ. Phys.-Chem. Soc., 46, No. 3, 442 (1914).

**OBSERVATION OF THE REACTIONS OF FORMATION OF  $MgAl_2O_4$  AND  $BeAl_2O_4$   
BY MEANS OF LUMINESCENCE SPECTRA**

A. K. Trofimov

(Presented by Academician A. N. Terenin, October 26, 1955)

As is well known, equimolar mixtures (1:1) of aluminum and magnesium oxides or of aluminum and beryllium oxides enter into chemical reaction with the formation of the spinels  $MgAl_2O_4$  and  $BeAl_2O_4$  when heated to high temperatures.

There has been a great amount of work devoted to the investigation of the reactions of formation of spinels, particularly of magnesium-aluminum spinel. K. M. Fedotyev and D. A. Bogdan [1], for example, using a crystallo-optical method showed that magnesium-aluminum spinel begins to form from the oxides at temperatures above 1200°. Yander [2], by an X-ray method, established the appearance of the first crystals of this spinel at a temperature of 920°. The reaction of the formation of beryllium-aluminum spinel and also the formation of  $MgAl_2O_4$  from  $BeAl_2O_4$  by a substitution reaction with  $MgO$  have been studied less.

Along with X-ray, crystallo-optical, chemical, and certain other methods for the study of the course of the reactions of formation of these spinels, spectra of the luminescence of crystallophosphors based on the substances participating in these reactions can be used. Line spectra of the luminescence of crystallophosphors activated with rare earths or chromium, as is well known, depend first of all on the crystallochemical nature of the base material and are very sensitive to changes in the latter. In the present work, this dependence was used for qualitative observation of the course of the reactions of formation of  $MgAl_2O_4$  and  $BeAl_2O_4$  with temperature. The materials participating in these reactions,  $MgO$ ,  $Al_2O_3$ ,  $MgAl_2O_4$ , and  $BeAl_2O_4$ , when activated with chromium, give phosphors with red luminescence ( $BeO$  does not give a phosphor with chromium), the luminescence spectra of which differ from each other in the location of the lines. Characteristic lines in the spectra of the luminescence of these materials are:  $MgO \cdot Cr$ , 698.3  $m\mu$ ;  $Al_2O_3 \cdot Cr$  (ruby), a doublet at 692.7 and 694.2  $m\mu$ ;  $MgAl_2O_4 \cdot Cr$ , a narrow doublet at 684.5 and 684.7  $m\mu$ ;  $BeAl_2O_4$ , a doublet at 677.0 and 678.7  $m\mu$ .

The magnesium, beryllium, and aluminum oxides, activated with chromium (0.2%), were prepared by the decomposition of the corresponding nitrates with added chromium nitrate, and were further calcined at a temperature of 1100° for 1 hour. The thus prepared oxides of magnesium and aluminum or of beryllium and aluminum were carefully mixed in an equimolar ratio, 1:1, pressed into small tablets, and calcined for 30 minutes at temperatures ranging from 600 to 1700° at intervals of 100°. Samples of an equimolar mixture (1:1) of  $BeAl_2O_4$  (this spinel was prepared from beryllium and aluminum oxides at a temperature of 1400°) and  $MgO$ , preactivated with chromium, (0.2%), were also prepared and calcined under these same conditions.

The samples were cooled with liquid air and excited with a mercury lamp, the radiation from which was passed through a solution of copper sulfate to eliminate the red end of the spectrum, and the spectra of the luminescence was photographed using a spectrograph with a diffraction grating. The dispersion of the apparatus was about 50  $\text{A/mm}$ .

The change in the luminescence spectra of the samples (Figures 1a, b, and c), calcined at different temperatures, indicated a crystallochemical transformation in them. The spectra of the luminescence of the samples consisting of a mixture of  $MgO \cdot Cr$  and  $Al_2O_3 \cdot Cr$  calcined at temperatures up to 1200° showed only the lines of the ruby doublet at 692.7 and 694.2  $m\mu$  (owing to the insufficient sensitivity of the photographic emulsion to the red region, the weak line for  $MgO \cdot Cr$  at 698.3  $m\mu$  was not present on the photograph). Calcination of these samples at 1200 to 1450° led to the appearance in the spectra of lines of the spinel

$\text{MgAl}_2\text{O}_4 \cdot \text{Cr}$  at 684.5 and 684.7  $\mu$ , an increase in the intensity of these lines and a weakening of the intensity of the  $\text{Al}_2\text{O}_3 \cdot \text{Cr}$  lines occurring as the calcination temperature was increased. Only the  $\text{MgAl}_2\text{O}_4 \cdot \text{Cr}$  lines remained in the spectra of the luminescence from the samples calcined above 1450°. Consequently, the crystalline structure of  $\text{MgAl}_2\text{O}_4$  appeared at a calcination temperature of 1200°, indicating initiation of the reaction between  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  at this temperature. This reaction was concluded, as follows from the cited luminescence spectra (Figure 1a), at about 1450°.

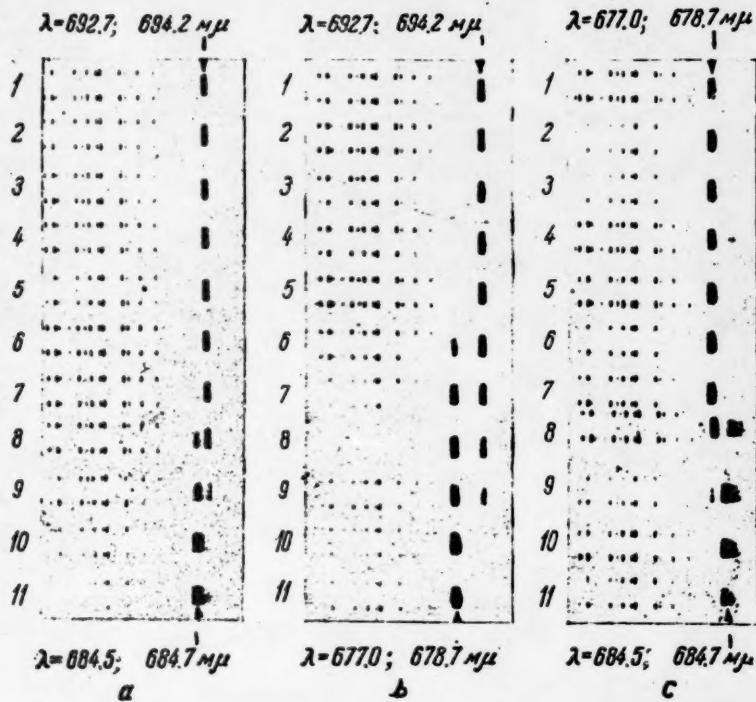


Fig. 1. Luminescence spectra of samples in equimolar mixture, activated with chromium and calcined for 30 minutes at temperatures of: 1) 600°, 2) 700°, 3) 800°, 4) 900°, 5) 1000°, 6) 1100°, 7) 1200°, 8) 1300°, 9) 1450°, 10) 1600°, 11) 1700° (spectrum comparison is neon). a)  $\text{Al}_2\text{O}_3 + \text{MgO}$ ; b)  $\text{Al}_2\text{O}_3 + \text{BeO}$ ; c)  $\text{BeAl}_2\text{O}_4 + \text{MgO}$

Spectra of the luminescence from samples of the mixture of  $\text{BeO} \cdot \text{Cr}$  and  $\text{Al}_2\text{O}_3 \cdot \text{Cr}$  calcined at temperatures up to 1100° consisted only of the lines of the ruby doublet at 692.7 and 694.2  $\mu$ , these lines being of constant intensity throughout this temperature interval. In the spectra of the samples of this mixture calcined at 1100 to 1450° there were observed both the  $\text{Al}_2\text{O}_3 \cdot \text{Cr}$  lines and the lines of the spinel  $\text{BeAl}_2\text{O}_4 \cdot \text{Cr}$  at 677.0 and 678.7  $\mu$ , the intensity of the first spectra decreasing and that of the second increasing as the calcination temperature of the mixture increased. At temperatures above 1450°, only the  $\text{BeAl}_2\text{O}_4 \cdot \text{Cr}$  lines remained in the luminescence spectra of the samples. Hence, it follows that the crystalline structure of the  $\text{BeAl}_2\text{O}_4$  spinel appeared at a temperature of 1100°, and that the amount of spinel increased as the temperature increased up to 1450°. Thus, the reaction between  $\text{BeO}$  and  $\text{Al}_2\text{O}_3$  with the formation of  $\text{BeAl}_2\text{O}_4$  began at 1100° and ended at about 1450° (Figure 1b).

For samples consisting of a mixture of  $\text{BeAl}_2\text{O}_4 \cdot \text{Cr}$  and  $\text{MgO} \cdot \text{Cr}$  calcined at a temperature below 1200°, the luminescence spectra showed only the  $\text{BeAl}_2\text{O}_4 \cdot \text{Cr}$  lines at 677.0 and 678.7  $\mu$ . Beginning at 1200°,  $\text{MgAl}_2\text{O}_4 \cdot \text{Cr}$  appeared in the spectra, the intensity of its lines increasing as the calcination temperature increased. Simultaneously with this, beginning at 1200° and continuing at higher temperatures, the intensity of the  $\text{BeAl}_2\text{O}_4 \cdot \text{Cr}$  spectral lines decreased. Only the spectra of  $\text{MgAl}_2\text{O}_4 \cdot \text{Cr}$  was observed for samples calcined above 1450°. Consequently, the formation of the magnesium-aluminum spinel according to the substitution reaction



began at 1200° and concluded at a temperature of about 1450° (Figure 1c).

The appearance of the crystalline structures of  $MgAl_2O_4$  and  $BeAl_2O_4$  at the above-indicated temperatures, established by spectra of the luminescence, were confirmed by radiograms of these same samples.

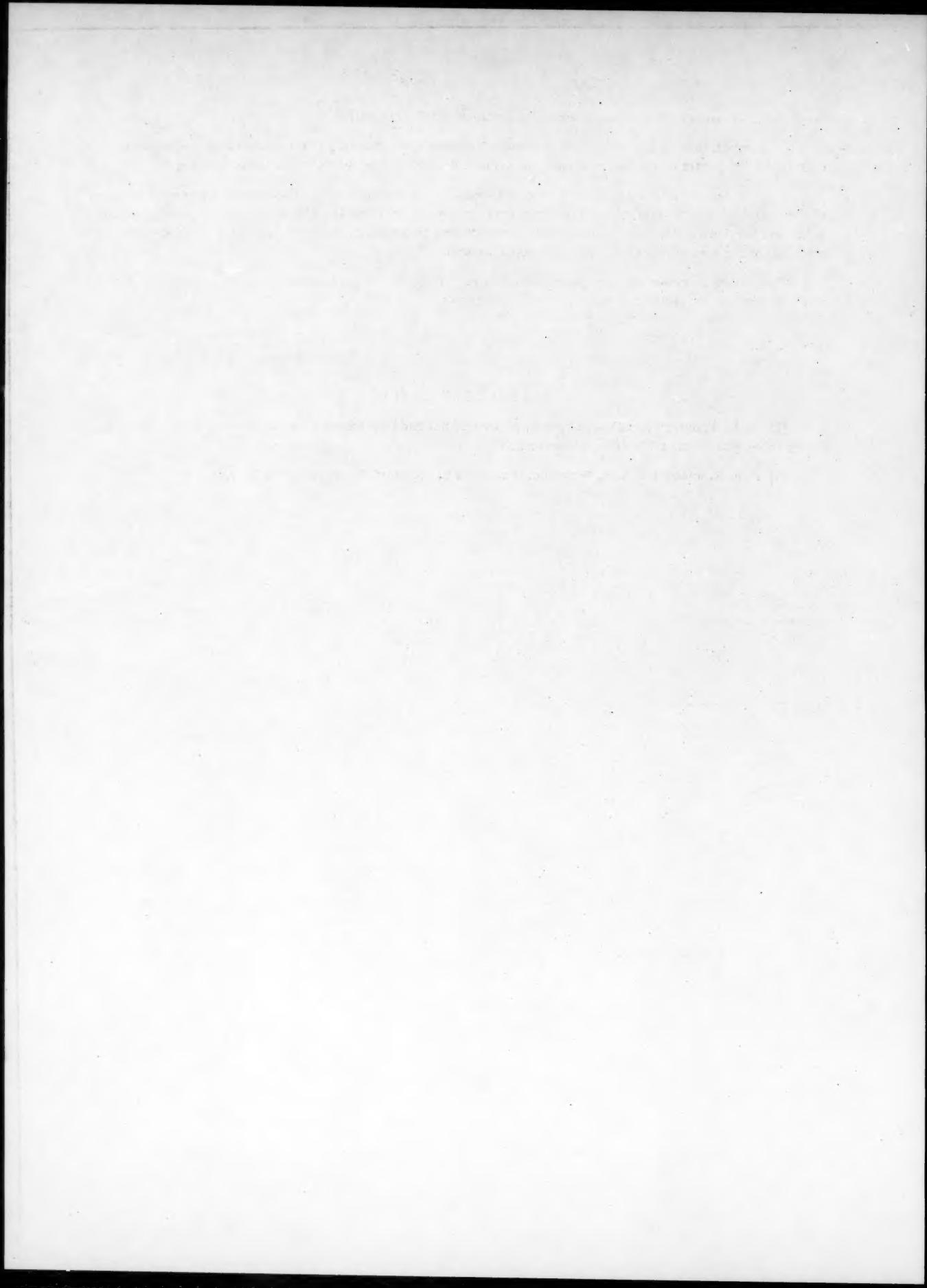
Thus, it was established that, by means of spectra of the luminescence of individual samples of mixtures of the oxides of magnesium and aluminum or beryllium and aluminum and also of a mixture of magnesium oxide and beryllium-aluminum spinel calcined at different temperatures, it is possible to observe the course of the reactions of the formation of  $MgAl_2O_4$  and  $BeAl_2O_4$  spinels.

The author expresses his deep appreciation to P. P. Feofilov for guidance in the work and to E. V. Stroganov and L. I. Kozhina for taking the radiograms of the samples.

Received October 20, 1955

#### LITERATURE CITED

- [1] K. M. Fedotyev and D. A. Bogman, Reports of the 2nd Conference on Experimental Mineralogy and Petrography, Acad. Sci. USSR Press, Moscow, 1937.
- [2] P. P. Budnikov and A. S. Berezhnoi, Reactions in the Solid Phase, Moscow, 1949.



INVESTIGATIONS IN THE FIELD OF THE SYNTHESIS AND TRANSFORMATIONS  
OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

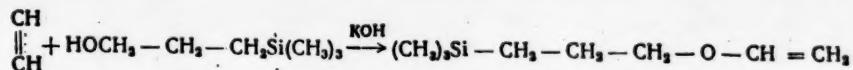
SYNTHESIS OF ORGANOSILICON ACETALS BASED ON THE VINYL ETHER OF  
 $\gamma$ -HYDROXYPROPYLTRIMETHYLSILANE, ORGANOSILICON ALCOHOLS, AND SILANOL

I. A. Shikhiev and N. V. Komarov

(Presented by Academician B. A. Kazansky, October 1, 1955)

The present work is a further development of the chemistry of simple vinyl ethers [1] containing silicon in their composition [2, 3].

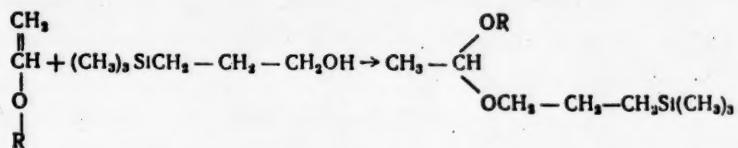
The organosilicon vinyl ether (vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane) was prepared by us [2] by a modification of the method of A. E. Favorsky and M. F. Shostakovskiy [4] according to:



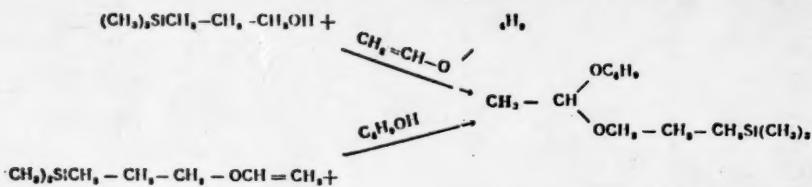
In the present work, vinylation of  $\gamma$ -hydroxypropyltrimethylsilane was carried out in a medium of dioxane and in the presence of 7.5% potassium alcoholate. The use of the latter permitted us to obtain yields of the organosilicon vinyl ether up to 63.0%.

In our previous investigations [5-9] it was first established that simple vinyl ethers of organic alcohols react with trialkyl- and also with alkyl(aryl)-silanols with the formation of the corresponding organosilicon acetals.

More recently, one of us [3] has synthesized mixed organosilicon acetals by the interaction of vinylalkyl ethers with  $\gamma$ -hydroxypropyltrimethylsilane according to

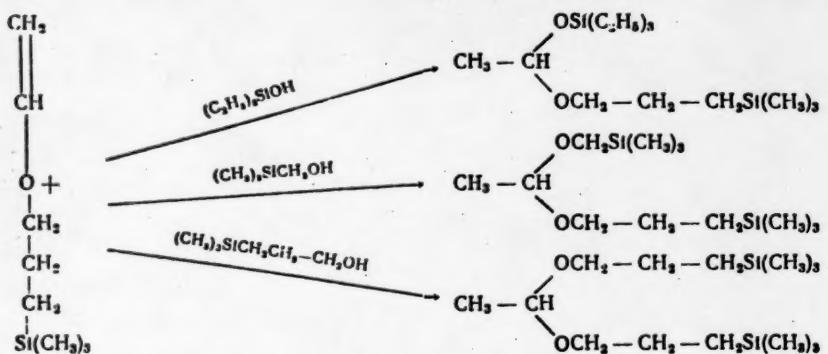


The structure of the thus prepared organosilicon acetals was shown by the synthesis of one of the representatives of this series by two routes:



The present investigation is devoted to a study of the reaction of the vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane with organosilicon alcohols and with a silanol. In this way were first obtained different symmetrical and unsymmetrical organosilicon acetals containing a silicon atom in both radicals.

The formation of the mixed and symmetrical organosilicon acetals can be represented as follows:



The structures of the acetals obtained follows from the synthesis.

The following starting materials were used in the syntheses of the organosilicon acetals: 1)  $\gamma$ -hydroxypropyltrimethylsilane; b. p. 62-63° (10 mm);  $d_4^{20}$  0.8408;  $n_D^{20}$  1.4298; 2) the vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane; b. p. 60° (18 mm);  $d_4^{20}$  0.8171;  $n_D^{20}$  1.4265; 3) trimethylsilylmethanol; b. p. 123° (733 mm);  $d_4^{20}$  0.8551;  $n_D^{20}$  1.4198; 4) triethylsilanol; b. p. 80° (30 mm);  $d_4^{20}$  0.8646;  $n_D^{20}$  1.4341.

Vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane. From 40 g (0.3 mole) of trimethylsilyl- $\gamma$ -propanol and 0.89 g (0.023 g-atom) of metallic potassium was obtained a solution of the potassium alcoholate, which, with 80 g of dioxane, was charged to a steel rotating autoclave of 0.5-liter capacity. The contents of the autoclave, at room temperature and with constant agitation, were saturated with acetylene.

There was a total of 24 atmospheres (9.88 g) of acetylene (theoretically required acetylene, 7.88 g) in the autoclave. The autoclave was heated at 150-160° for 5-6 hours. From the autoclave was discharged a dark liquid, which was separated from the tar by distillation. The distillate was washed 6 times with water, and the upper layer was successively dried with potash and metallic sodium. After two-fold distillation, there was obtained 30.2 g of product (63.2% of theoretical) having the following constants: b. p. 60-61° (18 mm);  $n_D^{20}$  1.4265;  $d_4^{20}$  0.8171;  $MR_D$  found 49.69; calculated for  $C_9H_{18}OSi$ ,  $MR_D$  50.10. The data obtained correspond to the vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane [2], which polymerizes in the presence of ferric chloride.

Di(trimethylsilylpropyl) acetal. 0.1 ml of 30% hydrochloric acid was added at room temperature

and with constant stirring to a mixture of 6.5 g (0.04 mole) of the vinyl ether of  $\gamma$ -hydroxypropyltrimethylsilane and 6.0 g (0.04 mole) of  $\gamma$ -hydroxytrimethylsilane. The temperature increased to 54°. The reaction mixture was heated for 30 minutes at 60-65° and left overnight, after which it was neutralized with potash and twice fractionated under vacuum. This resulted in the isolation of 7.9 g of product with a b.p. of 126-127° (6mm);  $d_4^{20}$  0.8549;  $n_D^{20}$  1.4350; found, MRD 88.67;  $C_{14}H_{34}O_2Si_2$  calculated MRD 89.75.

TABLE 1  
Properties of the Organosilicon Acetals Prepared

Formula		B.p., (°C)	$d_4^{20}$	$n_D^{20}$	MRD	C, %	H, %	Si, %	Yield, %
$\begin{array}{c} OSi(C_2H_5)_3 \\   \\ CH_3-CH \\   \\ OCH_2CH_2CH_2Si(CH_3)_2 \end{array}$	a	132°	0.8653	1.4362	87.83	58.58; 58.43	11.82; 11.89	19.06; 19.06	60.0
	b				87.84	57.87	11.80	19.31	
$\begin{array}{c} OCH_2Si(CH_3)_2 \\   \\ CH_3-CH \\   \\ OCH_2-CH_2-CH_2-Si(CH_3)_2 \end{array}$	a	107°	0.8408	1.4271	80.17	55.65; 55.71	11.52; 11.52	21.05; 20.75	58.4
	b	108°			80.49	54.90	11.52	21.38	
$\begin{array}{c} OCH_2-CH_2-CH_2-Si(CH_3)_2 \\   \\ CH_3-CH \\   \\ OCH_2-CH_2-CH_2-Si(CH_3)_2 \end{array}$	a	126°	0.8549	1.4350	88.67	57.67; 57.61	11.65; 11.66	19.03; 18.98	63.3
	b	127°			89.75	57.87	11.80	19.31	

Notes: a - found, b - calculated. \*at 9 mm; \*\*at 6 mm

The data obtained correspond to di(trimethylsilylpropyl) acetal. The yield was 63.3% of theoretical.

By a similar route were prepared two other organosilicon acetals, the constants of which are presented in Table 1.

#### LITERATURE CITED

- [1] M. F. Shostakovsky, Simple Vinyl Ethers, Acad. Sci. USSR Press, Moscow (1952).
- [2] M. F. Shostakovsky and I. A. Shikhiev, Bull. Acad. Sci. USSR, Div. Chem. Sci., 4, 745 (1954) (T. p. 643)\*.
- [3] I. A. Shikhiev, Proc. Acad. Sci. AzSSR, 11, 195 (1955).
- [4] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem., 13, I (1943).
- [5] M. F. Shostakovsky, I. A. Shikhiev and D. A. Kochkin, Bull. Acad. Sci. USSR, Div. Chem. Sci., 5, 941 (1953) (T. p. 837)\*.
- [6] M. F. Shostakovsky, K. A. Andrianov et al., Proc. Acad. Sci. USSR, 93, 681 (1953).
- [7] M. F. Shostakovsky, I. A. Shikhiev et al., Proc. Acad. Sci. AzSSR, 10, 473 (1954).
- [8] M. F. Shostakovsky, I. A. Shikhiev et al., J. Gen. Chem., 24, 2202 (1954) (T. p. 2175)\*.
- [9] M. F. Shostakovsky, Kh. I. Kondratyev and V. I. Belyaev, Proc. Acad. Sci. USSR, 100, 287 (1955).

N. D. Zelinsky Institute of Organic Chemistry  
Academy of Sciences of the USSR

Received June 29, 1955

\* T. p. = C. B. Translation pagination.



## THE ROLE OF COPPER IN THE REACTION BETWEEN ETHYL CHLORIDE AND SILICON

Associate Member of the Academy of Sciences, USSR

K. A. Andrianov, S. A. Golubtsov, I. V. Trofimova and R. A. Turetskaya

In the literature is described a series of works on the preparation of silicon-copper contact masses for the synthesis of methyl- and phenylchlorosilanes. It is indicated that the optimum amount of copper is from 10 to 20% for the reaction with methyl chloride [1] and about 50% for the reaction with chlorobenzene [2]; however, a systematic investigation of the effect of copper content on the catalytic activity of the silicon-copper contact mass has not been carried out.

We have studied this question using the reaction of silicon-copper alloy with ethyl chloride.

Literature data on the synthesis of ethylchlorosilanes is very limited. Yu. G. Mamedaliev and co-workers [3] have carried out a reaction between ethyl chloride and an alloy of ferrosilicon (80%) and copper (20%). According to the data of Rochow [4], in the reaction between ethyl chloride and silicon-copper contact mass, a mixture is formed which contains 26% diethyldichlorosilane, 27% ethyltrichlorosilane, and the main reaction product, silicon tetrachloride.

Mainly, our work was carried out according to a method of synthesis developed by us in 1952, which makes it possible to avert the formation of silicon tetrachloride and to direct the reaction chiefly toward the formation of diethyldichlorosilane.

150 g of pulverized alloy, which had been carefully dried in a stream of nitrogen, was charged to the reactor, after which a stream of ethyl chloride was passed through the alloy. The reaction products (a mixture of ethylchlorosilanes and excess unreacted ethyl chloride) were condensed in an Allihn condenser and collected in a receiver. After 4 hours of ethyl chloride flow, the synthesis was stopped (the alloy still completely retained its activity), and the reaction products were combined and fractionated in a 12-mm diameter column of 18 theoretical plates.

The following fractions were obtained: 1) a fraction boiling at 73-76° and containing mainly ethyldichlorosilane,  $(C_2H_5)_2SiHCl_2$ ; 2) a fraction boiling at 97-100° and representing a mixture of 70-90% ethyltrichlorosilane,  $C_2H_5SiCl_3$ , and 10-30% diethyldichlorosilane,  $(C_2H_5)_2SiHCl$ . The composition of the fraction was calculated from the results of analyses for chlorine content and for hydrogen combined with silicon; 3) a fraction boiling at 125-129°, mainly diethyldichlorosilane,  $(C_2H_5)_2SiCl_2$ ; 4) residue (chiefly, products of hydrolysis).

The composition of the intermediate fractions, the total amount of which did not exceed 20%, were calculated from analyses for chlorine content. The catalytic activity of the alloy was evaluated from the diethyldichlorosilane content of the reaction products, its formation proceeding according to the most efficient reaction  $2C_2H_5Cl + Si \longrightarrow (C_2H_5)_2SiCl_2$  which is not connected with the loss of organic radicals.

In Table 1 are presented experimental data on the dependence of the yield and composition of the reaction products on copper content of the series of samples of silicon-copper alloy tested by the described method. The results obtained show that the diethyldichlorosilane content of the mixture of ethylchlorosilanes gradually increased to 45-50% with a decrease in the copper content of the alloy from 70 to 5% (see Figure 1).

TABLE 1

## Effect of Copper Content on the Catalytic Activity of Silicon-Copper Alloys

Experi- ment No.	Copper content of the alloy, %	Mixture of ethyl- chlorosilanes ob- tained g	g/kg of alloy/ hour	Composition of ethylchlorosilane mixture				
				Ethyl- dichloro- silane	Ethyl- trichloro- silane	Diethyl- chloro- silane	Diethyl- dichloro- silane	Residue
1	70*	64	184	18	50	2	20	10
2	50	174	291	38	25	4	23	10
3	30	291	485	38	23	5	24	10
4	20	270	450	23	22	8	37	10
5	20	243	407	22	19	5	44	10
6	15	320	534	30	17	5	38	10
7	5	215	359	30	20	8	51	10
8	5	249	414	22	15	6	46	11

\* Reaction discontinued after 2 hours and 20 minutes

Considering the reasons for the increase in the catalytic activity of the alloy with a decrease in its copper content, it can be assumed that the increase in the yield of diethyldichlorosilane is connected with a decrease in the rate of secondary processes occurring during the synthesis, for example, thermal decomposition of diethylchlorosilane.

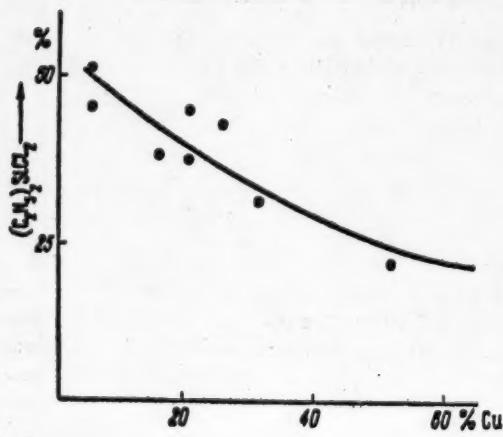


Fig. 1. Dependence of diethyldichlorosilane content on copper content of the alloy.

ture of chlorides, but the content of diethyldichlorosilane was practically unchanged. The formation of appreciable amounts of decomposition products, both solid (5-6% by weight of the mixture of ethylchlorosilanes) and gaseous (the amount of the latter was significantly higher when the decomposition was carried out over used catalyst) should be noted. According to the analytical data, the gaseous decomposition products contained 65-75% hydrogen, 10-20% ethylene, and up to 14% ethane.

Thus, it follows that secondary decomposition processes can play a specific role in the course of the synthesis of ethylchlorosilanes (especially in the final stage of the synthesis); however, we still find it impossible to explain the increase in catalytic activity of the silicon-copper alloys with a decrease in their copper content.

With the aim of verifying the effect of decomposition under synthesis conditions on the amount and composition of the reaction products, we passed through the reactor, which was charged with 80 g of silicon-copper alloy, a mixture of ethylchlorosilanes having the following composition: ethyldichlorosilane 23%, ethyltrichlorosilane 24%, diethylchlorosilane 5%, diethyldichlorosilane 38%, residue 10%.

Passing through the reactor, the mixture was condensed in an Allihn condenser, and the gaseous decomposition products were collected in a gasometer. The experimental conditions (temperature, contact time of the mixture of chlorosilanes with the alloy) corresponded with the synthesis conditions. In Table 2 are presented the results of experiments carried out using 20% and 5% silicon-copper alloy, both fresh and used.

The data obtained show that thermal decomposition of reaction products under synthesis conditions proceeds to an insignificant extent. There was observed some decrease in the content of ethyldichlorosilane and an increase in the content of ethyltrichlorosilane in the mixture.

TABLE 2

Decomposition of a Mixture of Ethylchlorosilanes Over Silicon-Copper Alloy

Experiment No.	% Copper in the fed alloy	g of mixture in the fed alloy	Obtained						Loss during fractionation, %		
			Decomposition Products		Composition of liquid products, %						
			Solid, g	Gas, liters	Liquid, g	Ethyldichlorosilane	Ethytrichlorosilane	Diethylchlorosilane	Diethyl dichlorosilane	Residue	
1	20 *	126.4	6.0	0.55	116.2	22	26	5	39	8	3
2	20 **	106.3	5.5	2.32	97.5	16	32	3	37	12	8
3	5 *	112.9	5.5	0.95	104.3	19	27	3	40	12	Less than 1
4	5 **	107.3	5.0	1.17	100.0	19	27	4	37	10	6

\* Fresh alloy

\*\* Alloy used for 4 hours

A second cause of this phenomenon could be an increase in the intensity of side reactions connected with the decomposition of ethyl chlotide and the formation of large amounts of gaseous products with an increase in the copper content of the alloy. With the aim of clarifying this question, 1-hour experiments, with quantitative recovery of gaseous reaction products, were carried out on the synthesis of ethylchlorosilanes over alloys having copper contents from 5 to 50% (Table 3).

TABLE 3

Effect of Copper Content of Silicon-Copper Alloys on the Decomposition of Ethyl Chloride

Experiment No.	% Copper in alloy	g of ethylchlorosilanes obtained	Composition of the ethylchlorosilane mixture					Volume of gas, liters	Gas composition, %				ng/nd
			Ethyldichlorosilane	Ethytrichlorosilane	Diethylchlorosilane	Diethyl dichlorosilane	Residue		C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub>	HCl	
1	50	55.3	42	22	6	21	9	9.5	54	10	35	1	1,68
2	30	64.9	25	25	4	36	10	7.8	69	8	23	—	0.83
3	25	48.8	18	20	5	48	9	8.3	69	9	22	0.6	0.87
4*	5	59.4	20	12	6	52	10	2.4	25	21	48	6	0.17
5	100	Decomposed on the copper					0.6	17	34	31	18		

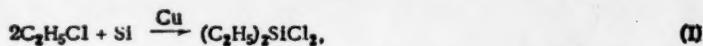
\* 1.5-Hour synthesis

The data presented in Table 3 show that, at high copper contents in the alloy, along with a decrease in diethyldichlorosilane content, a sharp increase in the amount of gases formed (ethylene, hydrogen) takes place. But active catalysts with low copper contents, however, were characterized by a high percentage of diethyl dichlorosilane in the ethylchlorosilane mixtures and by the formation of considerably smaller amounts of gas. It is very interesting to note that the ratio of the number of moles of ethyl chloride consumed in the formation of ethylene and ethane ( $n_g$ ) to the number of moles of ethyl chloride consumed in the formation of diethyldichlorosilane ( $n_d$ ) presented in the last column of Table 3, increased proportionally to the copper content of the alloy, and this ratio can serve as an indicator of the catalytic activity of the contact mass.

The data from Experiment 5, Table 3, show that, when ethyl chloride is passed through pure electrolytic copper powder, the products are decomposed into ethylene, hydrogen chloride, ethane and hydrogen.

On the basis of the experimental data presented, it is possible to come to the following conclusions concerning the course of the reaction between ethyl chloride and silicon-copper alloys containing different amounts of copper.

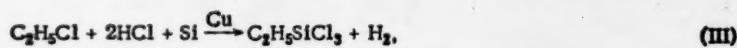
Along with the main course of the reaction



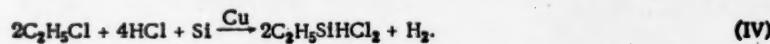
leading to the formation of the most valuable product — diethyldichlorosilane — the side process of the catalytic decomposition of ethyl chloride in the presence of copper occurs:



If, in the case of pure copper, the hydrogen chloride formed is liberated chiefly in the free form, then, in the reaction with silicon-copper alloy, it enters into the reaction leading to the formation of ethyltrichlorosilane



and ethyldichlorosilane



The hydrogen liberated during reactions (III) and (IV) can partially hydrogenate the ethylene with the formation of ethane. The presence of Reactions (II) — (IV) can be verified, first, by the insignificant amount of hydrogen chloride in the gaseous reaction products and, second, by the formation of large amounts of ethyldichlorosilane and ethyltrichlorosilane in the same experiments where the amount of gas formed was a maximum (Experiment No. 1, Table 3).

Thus, we consider it possible to assume that the copper plays a double role in the reaction of ethyl chloride with silicon-copper alloy: it catalyzes the synthesis of diethyldichlorosilane according to Reaction (I), and, on the other hand, it contributes to the decomposition of ethyl chloride with the formation of ethylene, hydrogen, ethane, ethyldichlorosilane, and ethyltrichlorosilane according to Reactions (II) — (IV), whereupon, an increase in the copper content of the alloy decreases the selective property of the alloy for Reaction (I) and increases it for Reactions (II) — (IV).

Received November 21, 1955

#### LITERATURE CITED

- [1] U. S. Patents 2,380,996 and 2,380,999, Class 260-607 (1945).
- [2] E. G. Rochow and V. F. Gilliam, J. Am. Chem. Soc., 67, 1772 (1945).
- [3] Yu. G. Mamedaliev, et al., Proc. Acad. Sci. AzSSR, 6, 365 (1950); 8, 153 (1952).
- [4] E. G. Rochow, J. Am. Chem. Soc. 67, 963 (1945).

## ALKYLATION OF META-, ORTHO-, AND PARA-CRESOLS WITH ACETLYENE

V. L. Vaisser and A. M. Polikarpova

(Presented by Academician A. V. Topchiev, November 21, 1955)

m-Cresol (b.p. 199-200°) was alkylated with acetylene in a reactor into which was charged in all experiments 20 g of cresol, 50 ml of methyl alcohol, various amounts of  $H_3PO_4BF_3$  catalyst, and 1-2 g of mercuric oxide. Acetylene from a cylinder was charged at a rate of 1 to 4 liters/hour for a period of from 0.5 to 3 hours and at various reaction temperatures. After the conclusion of the reaction, the alkylate was extracted with ether, and the upper layer was decanted and washed to a neutral reaction. The ether was distilled off, and the residue was steam distilled in order to remove the unreacted m-cresol. The product remaining in the flask solidified on cooling, and, upon grinding, a light yellow powder was obtained which was soluble in alkali, alcohol, hot benzene, and acetic acid. Experiments with o- and p-cresol were carried out similarly. The yield of alkylate differed depending on the concentration of catalyst, the reaction temperature, the acetylene feed rate, and the duration of reaction (see Table 1).

The variation in alkylate yield with catalyst concentration, other conditions being equal, is shown in Table 2.

As seen from Table 2, an increase in the concentration of catalyst from 1/20 to 1/10 produced an insignificant increase in the yield of alkylate (5%); an increase in the concentration to 1/5 increased the yield 25%, and, finally, a further increase in catalyst concentration decreased the yield of alkylate. The optimum concentration was 1/5 - the same as in the similar alkylation of phenol in alcoholic solution [1] and differing from the optimum catalyst concentration in the alkylation of phenol in aqueous solution, 2/5 [2].

m-Cresol alkylates considerably easier than phenol, as can be seen by comparing the 4 experiments carried out under the same conditions of concentration, temperature, etc. (see Table 3).

The effect of temperature on the alkylation of m-cresol can be seen from Table 4.

The optimum temperature was 25-30°, which is the temperature established in the process by the reaction itself (without heating or cooling). A two-fold increase in temperature produced almost no change in alkylate yield; lowering the temperature to 5-8° decreased the yield by 20-30%.

In the alkylation of phenol, both in aqueous [1] and in alcoholic [2] solution, the optimum temperature was 65°; this also confirms that m-cresol alkylates easier than phenol.

The variation in alkylate yield with acetylene feed rate at otherwise equal conditions is presented in Table 5. As seen from the table, an increase in acetylene feed rate from 1 to 4 liters/hour doubled the yield of alkylate calculated on the basis of the cresol, and reduced it by 50% calculated on the basis of acetylene. Such contradictory data can be explained by the fact that, with an increase in the acetylene feed rate, much of the acetylene leaves the sphere of the reaction and does not have time to react; therefore, yields are more correctly based on the cresol, which remains in the reactor throughout the alkylation.

The variation in alkylate yield with duration of reaction, other conditions being the same, is shown in Table 6. An increase in reaction time from 0.5 to 3 hours increased the alkylate yield, based on cresol, by a factor of 4. The optimum reaction time was 2 hours. Here, also, was observed the same contradiction: with an increase in the reaction time, the yield, based on acetylene, decreased. A similar phenomenon occurs in the alkylation of phenol in alcoholic solution [1].

TABLE 1

Alkylation of m-, o-, and p-Cresol

Expt. No.	Catalyst, ml	Temp., °C	Acetylene feed rate, liters / hour	Duration of reaction, hours	Alkylate obtained, g	Yield, %	
						Based on acetylene	Based on cresol
<b>m-Cresol</b>							
1	20	55-60	3	2	21	33	94
2	20	55-60	—	—	—	—	*
3	20	55-60	—	—	—	—	*
4	20	25-30	2	2	13	30	58***
5	20	25-40	3	2	19	29	85
6	10	55-60	3	2	21	32	94
7	10	25-30	3	2	22	34	98
8	10	5-8	3	2	14	22	62***
9	10	55-60	3	2	22	34	98**
10	5	55-60	3	2	16	25	72
11	2.5	55-60	3	2	15	23	67
12	10	55-60	3	1	13	41	58
13	10	55-60	3	0.5	5.5	34	24
14	10	55-60	3	3	22	23	98
15	10	55-60	1	2	11	51	49
16	10	55-60	2	2	16	37	72
17	10	55-60	4	2	22	26	98
<b>o-Cresol (m.p. 31.5°)</b>							
18	20	65-70	3	2	20	31	89
19	10	65-70	3	2	11	17	49
<b>p-Cresol (m.p. 36°)</b>							
20	20	65-70	3	2	22	34	98

\* Expts. Nos. 2 and 3 were carried out as controls, without acetylene, in order to determine that methyl alcohol does not react with cresol under the given conditions. No such reaction was observed. Distillation of pure m-cresol from the solution in other experiments constitutes a similar check.

\*\* Expt. No. 9, 1 g of mercuric oxide was added instead of 2 g.

\*\*\* The temperature of 25-30° was established during the process by the reaction itself; the temperature of 55-60° was obtained by heating on a water bath, the temperature 5-8° by cooling.

TABLE 2

Expt. No.	Catalyst concentration*	Alkylate yield, %	
		Based on acetylene	Based on cresol
1	2/5	33	94
6	1/5	32	94
9	1/5	34	98
10	1/10	25	72
11	1/20	23	67

\* The catalyst concentration is given as the ratio of the volume of catalyst (acid) to the volume of methyl alcohol.

TABLE 3

Expt. No.	Substance alkylated	Yield, %
1	Cresol	94
306	Phenol	45 [1]
6	Cresol	94
281	Phenol	55 [1]

Comparative yield data from 3 experiments in which m-, o-, and p-cresol were alkylated are presented in Table 7.

Comparative yield data on the alkylation of m-cresol, toluene, and phenol in alcoholic solution and under almost the same conditions are presented in Table 8.

TABLE 4

Expt. No.	Temp., °C	Yield %	
		Based on acetylene	Based on cresol
6	55-60	32	94
7	25-30	34	98
8	5-8	22	62

TABLE 5

Expt. No.	Reaction time, hours	Yield %	
		Based on acetylene	Based on cresol
15	1	51	49
16	2	37	72
6	3	32	94
17	4	26	98

TABLE 6

Expt. No.	Reaction time, hours	Yield %	
		Based on acetylene	Based on cresol
13	0.5	34	24
12	1	41	58
6	2	32	94
14	3	23	98

TABLE 7

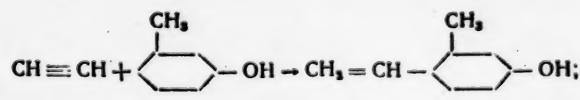
Expt. No.	Substance alkylated	Yield, in %, based on cresol
20	n-Cresol	98
1	m-Phenol	94
18	o-Cresol	89

TABLE 8

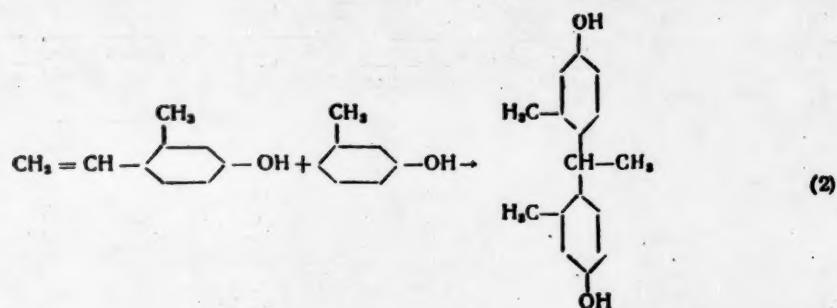
Expt. No.	Substance alkylated	Catalyst concentration	Temp., °C	Reaction time, hours	Overall yield %
14	m-Cresol	1/5	55-60	3	98
-	Toluene	1/5	55-60	3	31
281	Phenol	1/5	60-65	3	55 [1]
1	m-Cresol	2/5	55-60	2	94
-	Toluene	2/5	50-65	3	34
304	Phenol	2/5	65	3	44 [1]

It is seen from the table that these substances can be arranged in the following order with respect to their activity in alkylation reactions: m-cresol > phenol > toluene; it is also seen that the total yield of phenol and toluene alkylates was 84-88% of the yield of m-cresol. This, in all probability, is connected to some extent with the higher orienting effect of the  $\text{CH}_3$  radical and the OH functional group in the molecule of m-cresol, in which each C - H bond is subjected to the double effect of the methyl radical and the hydroxyl group.

The alkylation of cresols proceeds in two stages: in the first vinylcresol is obtained according to Equation (1):



in the second stage, according to Equation (2):



a substance, identified by us as ethylidene di-cresol [*1,1-bis(4-hydroxy-2-methylphenyl)ethane*],  $C_{18}H_{18}O_2$  was obtained.

This structure was confirmed by:

1) Elemental analysis: m-cresol:

Found %: C 79.7; 78.1; H 7.27; 7.2; O 13.03; 14.7  
 Calculated %: C 79.4 H 7.44; O 13.18.

2) Determination of the hydroxyl groups by the method of Tserevitinov-Chugaev: found, %: OH, 15.4; calculated, %: 14.0.

3) Determination of the molecular weight by the Rast method: found 254 and 252; Calculated 242.

Vinylcresol or polymers of vinylcresol were not detected; in all probability, the rate of Reaction 2 is considerably greater than the rate of possible vinylcresol polymerization reactions.

I. M. Gubkin, Moscow  
 Institute of Petroleum

Received November 11, 1955

LITERATURE CITED

- [1] V. L. Vaisser and A. M. Polikarpova, Proc. Acad. Sci. USSR, 97, No. 4 (1954).
- [2] V. L. Vaisser, Proc. Acad. Sci. USSR, 103, No. 5 (1955).

## ISOMERIZATION OF MONOOLEFINIC HYDROCARBONS BY THE ACTION OF CALCIUM AMIDE

I. V. Gostunskaya, N. I. Tyunkina and Academician B. A. Kazansky

B. A. Kazansky and N. F. Glushnev observed the isomerization of dienes with isolated double bonds into dienes with a conjugated system of double bonds during reduction by calcium hexaammoniate [1]. We succeeded in showing that the isomerizing action was due, not to calcium hexaammoniate itself, but to the calcium amide formed by decomposition of the hexaammoniate  $\text{Ca}(\text{NH}_3)_6 \rightarrow \text{Ca}(\text{NH}_2)_2 + 4\text{NH}_3 + \text{H}_2$ , and that the isomerization reaction in the presence of calcium amide is catalytic [2].

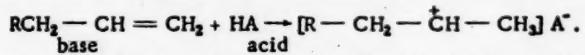
The present work was undertaken with the aim of a more detailed study of this reaction as applied to the isomerization of monoolefins of the aliphatic series. Olefins used in the investigation were 2-methylbutene-1, 3-methylbutene-1, hexene-1, 2,3-dimethylbutene-1, 2,3-dimethylbutene-2, 2,5-dimethylhexene-2, and 2,5-dimethylhexene-3. Isomerization was carried out at 70° and, for 2,5-dimethylhexene-3, at a temperature of 120° as well.

Study of the composition of the isomerization products showed that, under the conditions investigated, isomerization of the olefins proceeded with a shift of the double bond both from the end of the hydrocarbon chain to the center and from the center of the chain to the end, so that, in a mixture of isomers, the isomer with the greatest degree of substitution at the double bond predominated. For example, in the mixture of isopentenes, 2-methylbutene-2 predominated; in the mixture of 2,5-dimethylhexenes, 2,5-dimethylhexene-2 predominated; etc.

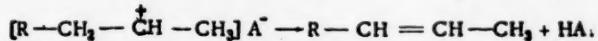
In order to compare the ease with which monoolefins of different structures isomerized, the relative rates of isomerization of the olefins were determined. Hexene-1, which has a normal structure, isomerized at a far greater rate than a hexene having an isostructure, 2,3-dimethylbutene-1. A comparison of the relative isomerization rates of olefins differing only in the position of the double bond in the molecule shows that, in all cases, that isomer in which the allylic carbon had the least degree of substitution isomerized at the highest rate. For example, 2-methylbutene-1 isomerized more rapidly into 2-methylbutene-2 than did 3-methylbutene-1, etc.

The isomerization of olefinic hydrocarbons under the influence of calcium amide and of potassium and sodium amides, which has been observed by a number of authors [2,3,5], is a rather unexpected phenomenon, since the amides of the alkali and alkaline earth metals are strongly basic and the majority of the known isomerization catalysts have an acid nature.

According to the currently most favored concept of the mechanism of the isomerization of olefins in the presence of acid catalysts, intermediate carbonium ions are formed:



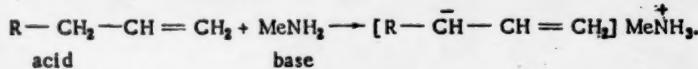
The subsequent reverse transfer of a proton from the carbonium ion to the catalyst can lead to a shift of the double bond:



In the reaction forming the carbonium ion, the olefin, adding a proton, acts as a base. However, according to current ideas in the field of the theory of acids and bases, first expressed by Brønsted, Lowry and Lewis and successfully developed in recent years by Shatenshtein [5-14], hydrocarbons can take the part either of weak bases or weak acids depending on the medium and the nature of the agents reacting with them.

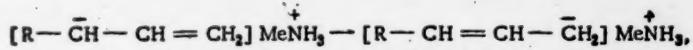
Studying isotope exchange in hydrocarbons of different classes, Shatenshtein showed that hydrocarbons in liquid ammonia in the presence of potassium amide act as weak acids, the strength of which can be characterized by the rate of the isotope exchange.

It can be assumed that, in isomerization reactions under the influence of metal amides, olefins exhibit their acid properties and have the capacity of splitting off a proton with the formation of an intermediate carbanion (an ion with a trivalent negative carbon):



In the formation of a carbanion, it is most probable that a hydrogen in the allylic position will be split off first; this is evident from the work of Shatenshtein on isotope exchange in olefins [5,10] and the work of Morton on the metallation of olefins [15-19] in which it was shown that the hydrogen atom in the allylic position possesses the greatest mobility.

In the carbanion formed, a shift of the negative charge to the double bond with the formation of a new carbanion is probable:

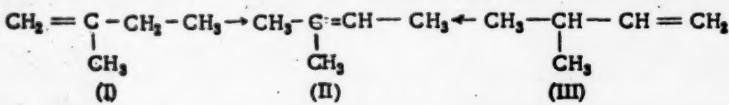


and, after the addition of a proton, the new carbanion yields an olefin having the double bond in a new position:



Such a reaction mechanism explains the catalytic nature of the reaction and the difference in isomerization rates of olefins of different structure under the influence of calcium amide.

Actually, according to the data of Morton [15] and Shatenshtein [13], the mobility of an allylic hydrogen decreases on passing from a methyl to a methyldiene group:  $\text{CH}_3 > \text{CH}_2 > \text{CH}$ ; hence, the high rate of isomerization of 2-methylbutene-1 (I) into 2-methylbutene-2 (II) compared to the rate of isomerization of 3-methylbutene-1 (III) into 2-methylbutene-2 (II) can be explained by the fact that in the first olefin the allylic hydrogen is in a  $\text{CH}_2$  group and possesses greater mobility than the allylic hydrogen in the second amylene (III) where it is in a  $\text{CH}$  group:



That the rate of isomerization of 2,3-dimethylbutene-2 into 2,3-dimethylbutene-1 is higher than the rate of the reverse reaction and that the rate of isomerization of 2,5-dimethylhexene-2 into 2,5-dimethylhexene-3 is higher than the rate of the isomerization of the 3-alkene into the 2-alkene can be explained in a similar manner.

## EXPERIMENTAL

Properties of the monoolefins investigated. 3-Methylbutene-1: b.p.  $20.2^\circ$  (760 mm);  $n_D^{20} 1.3645$ ,  $d_4^{20} 0.6269$ . 2-Methylbutene-1: b.p.  $31.3^\circ$  (760 mm);  $n_D^{20} 1.3772$ ,  $d_4^{20} 0.6500$ . Hexene-1: b.p.  $63.3^\circ$  (760 mm);  $n_D^{20} 1.3881$ ,  $d_4^{20} 0.6733$ . 2,3-Dimethylbutene-1: b.p.  $55.5^\circ$  (760 mm);  $n_D^{20} 1.3899$ ,  $d_4^{20} 0.6765$ . 2,3-Dimethylbutene-2: b.p.  $72.7^\circ$  (760 mm);  $n_D^{20} 1.4130$ ,  $d_4^{20} 0.7080$ . 2,5-Dimethylhexene-2: b.p.  $112.6^\circ$  (760 mm);  $n_D^{20} 1.4155$ ,  $d_4^{20} 0.7224$ . 2,5-Dimethylhexene-3: b.p.  $101-101.2^\circ$  (760 mm);  $n_D^{20} 1.4048$ ,  $d_4^{20} 0.6999$ .

Study of the composition of the products of the isomerization of monoolefinic hydrocarbons. The isomerizations were carried out by heating the olefin (or a mixture of two isomers) with calcium amide, using an olefin-to-amide mole ratio of 1:0.33, until there was no further change in the index of refraction of the mixture, i.e., to constant composition of the mixture, at a temperature of  $70^\circ$  and, for 2,5-dimethylhexene-3, at a temperature of  $120^\circ$  also. The composition of the isomerization products was determined by distilling the isomerizates in a column of 70 theoretical plates and examining the Raman spectra of the fractions obtained\*. The composition of the products of the isomerization of olefins are presented in Table 1.

\*The spectra were taken by E. G. Treshchova, V. T. Aleksanyan and Kh. E. Sterin.

TABLE 1

Initial monoolefin	Temp., °C	Catalyzate composition	
		Monoolefin	Content, %
3-Methylbutene-1	70	3-Methylbutene-1	8
		2-Methylbutene-2	92
2-Methylbutene-1	70	2-Methylbutene-1	11
		2-Methylbutene-2	89
Hexene-1	70	Hexene-1	10
		Hexene-2 + hexene-3	90
2,3-Dimethylbutene-1	70	2,3-Dimethylbutene-1	13
		2,3-Dimethylbutene-2	87
2,5-Dimethylhexene-2	70	2,5-Dimethylhexene-1	18.6
		2,5-Dimethylhexene-2	74.6
		2,5-Dimethylhexene-3	7.0
2,5-Dimethylhexene-3	120	2,5-Dimethylhexene-1	4.3
		2,5-Dimethylhexene-2	81.7
		2,5-Dimethylhexene-3	14.0

Study of the relative rates of isomerization of monoolefinic hydrocarbons. Monoolefins were passed through a catalyst tube charged with calcium amide at a temperature of 70°, and at 120° in the case of 2,5-dimethylhexene-3, and at a space rate of 0.2. The per cent conversion of the monoolefins was calculated from the change in the refractive index of the hydrocarbon resulting from the isomerization. This method of determining composition, which is applicable to binary mixtures, could be used in the present case, since it was shown that isomerization of amylenes and of 2,3-dimethylbutenes gave binary mixtures, and in the isomerization of 1-hexene and octenes, although a mixture of three isomers was formed, the constants of two of them practically coincided (hexene-2 and hexene-3; 2,5-dimethylhexene-1 and 2,5-dimethylhexene-2); therefore, the composition of such mixtures could be calculated from refractive index similarly to the composition of binary mixtures. In Table 2 are presented data on the content of isomerization products in the catalyzate, and the per cent of equilibrium concentration, calculated from the data on Table 1, is also given.

TABLE 2

Initial monoolefin	Temperature, °C	Isomerization products	Content of isomerization product, %	
			In the cat- alyzate	Recalculated on the basis of equi- librium concen- tration
2-Methylbutene-1	70	2-Methylbutene-2	62.2	70.5
3-Methylbutene-1	70	2-Methylbutene-2	55.0	60.1
Hexene-1	70	Hexene-2 + hexene-3	90	100
2,3-Dimethylbutene-1	70	2,3-Dimethylbutene-2	1.5	1.7
2,3-Dimethylbutene-2	70	2,3-Dimethylbutene-1	3.5	27
2,5-Dimethylhexene-2	70	2,5-Dimethylhexene-3	8	100
2,5-Dimethylhexene-3	70	No change	-	-
2,5-Dimethylhexene-3	120	2,5-Dimethylhexene-1 + 2,5-dimethylhexene-2	02	95

#### LITERATURE CITED

- [1] B. A. Kazansky and N. F. Glushnev, Bull. Acad. Sci. USSR, Div. Mech. Eng. Sci. 1065 (1938).
- [2] I. V. Gostunskaya and B. A. Kazansky, J. Gen. Chem., 25, 1995 (1955) (T.p. - 1943)\*.
- [3] W. Hückel and H. Bretschneider, Ann. 540, 172 (1939).
- [4] A. I. Birch, J. Chem. Soc. 1642 (1947).
- [5] A. I. Shatenshtein, L. N. Vasilyeva, et al., Proc. Acad. Sci. USSR, 85, 381 (1952).
- [6] A. I. Shatenshtein, The Theory of Acids and Bases, Moscow, 1949.
- [7] A. I. Shatenshtein, Proc. Acad. Sci. USSR, 70, 1029 (1950).
- [8] A. I. Shatenshtein, N. M. Dykhno, et al., Proc. Acad. Sci. USSR, 79, 479 (1951).
- [9] A. I. Shatenshtein, J. Phys. Chem., 25, 1206 (1951).
- [10] A. I. Shatenshtein, Progr. Chem., 21, 914 (1952).
- [11] A. I. Shatenshtein, L. I. Vasilyeva and N. M. Dykhno, J. Phys. Chem., 28, 193 (1954).
- [12] A. I. Shatenshtein and L. I. Vasilyeva, Proc. Acad. Sci. USSR, 95, 115 (1954).
- [13] A. I. Shatenshtein, Progr. Chem., 24, 377 (1955).
- [14] A. I. Shatenshtein, Questions of Chemical Kinetics, Catalysis, and Reactivity, Acad. Sci. USSR Press, 1955, p. 699.
- [15] A. A. Morton, M. L. Brown, et al., J. Am. Chem. Soc. 67, 2224 (1945).
- [16] A. A. Morton, M. L. Brown and E. Magat, J. Am. Chem. Soc., 69, 161 (1947).
- [17] A. A. Morton and H. C. Wohlers, J. Am. Chem. Soc. 69, 167 (1947).
- [18] A. A. Morton and M. E. T. Holden, J. Am. Chem. Soc., 69, 1675 (1947).
- [19] A. A. Morton, F. D. March, et al., J. Am. Chem. Soc. 72, 3785 (1950).

---

\*(T.p. = C. B. Translation pagination)

THE QUESTION OF THE QUANTITATIVE CHARACTERIZATION OF THE  
TRANS-EFFECT IN COMPLEX COMPOUNDS OF TETRAVALENT PLATINUM

O. E. Zvyagintsev and E. F. Karandasheva

(Presented by Academician I. I. Chernyaev, November 26, 1955)

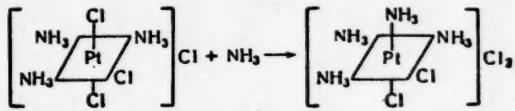
Investigation of the kinetics of inner sphere substitution reactions is one of the methods for the quantitative characterization of the trans-effect of addenda of complex compounds.

It has been previously shown by us [1] that a study of the kinetics of substitution reactions of monoammines of divalent platinum with pyridine makes possible a quantitative comparison of the trans-activity of certain inner sphere substituents. It was of interest to trace the extent to which the trans-effect is exhibited in substitution reactions of compounds of tetravalent platinum. Up to the present, the kinetics of reactions involving substitution in compounds of Pt(IV) have not been studied by anyone.

A. A. Grinberg, L. E. Nikolskaya and G. A. Shagisultanova [2] carried out experiments investigating the rate of isotope exchange in derivatives of Pt(IV) of the type  $K_2[PtX_6]$ , and they showed that, in derivatives of Pt(IV), exchange proceeds at a measurable rate, but the order of the complex compounds arranged with respect to rate of isotope exchange depended on the nature of the coordinated anions in the same manner as in the case of Pt(II). However, the isotope exchange reaction and the substitution of addenda differ substantially from one another.

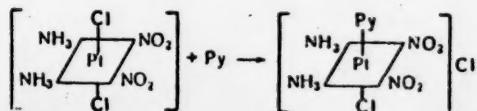
Triammines of the composition  $[(NH_3)_3PtCl_2X]Cl$ , and  $[EnPtNH_3NO_2ClX]Cl$  and Blomstrand salts  $[(NH_3NO_2)_2 - PtClX]Cl$ , where X is Cl, Br, or  $NO_2$ , were selected as subjects of the present investigation.

I. I. Chernyaev [3] showed that in the action of ammonia on a triammine, the Cleve reaction proceeds according to the principle of the trans-effect, that is, one of the chlorines in the coordinate  $Cl - Pt - Cl$  is substituted by ammonia.



It can be assumed that the action of pyridine on a triammine of such structure will substitute only one chlorine or bromine in the coordinates  $Cl - Pt - Cl$ ,  $Cl - Pt - Br$ . Analysis of the Cleve tetraammines of the compositions  $[(NH_3)_3PtClPyCl]Cl$ , and  $[(NH_3)_3PtClBrPy]Cl$  obtained as a result of the action of pyridine on triammines confirmed the assumed course of the reaction.

A. M. Rubinshtein [4] studied the action of pyridine on the Blomstrand salt  $[(NH_3NO_2)_2PtCl_2]Cl$ , and showed that this reaction also proceeds according to the principle of the trans-effect.

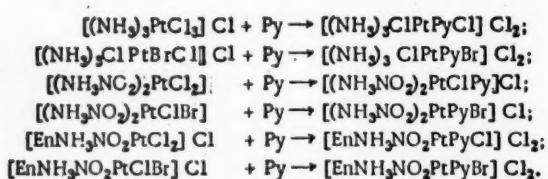


In the action of pyridine on the Blomstrand salt  $[(\text{NH}_3\text{NO}_2)_2\text{PtClBr}]$ , the reaction proceeds similarly with the reactive coordinate  $\text{Cl}-\text{Pt}-\text{Br}$ . The reactions of salts of the compositions  $[\text{EnPtNH}_3\text{NO}_2\text{Cl}_2]\text{Cl}$  and  $[\text{EnPtNH}_3\text{NO}_2\text{BrCl}]\text{Cl}$  also proceed only at one coordinate.

TABLE 1

Reaction	25°	30°	35°	40°	E, cal.
	$K \cdot 10^4$ liters./mole.sec.				
	1.88	3.42	6.05	10.56	21250
	5.20	9.00	15.0	25.0	19300
	0.66	1.20	2.18	3.85	21770
	2.03	3.66	6.50	11.40	21260
	4.39	7.56	12.8	20.9	19270
	0.86	1.59	2.88	5.04	21780
	2.82	5.05	9.0	15.58	21100
	7.59	13.06	22.0	36.0	19200
	1.26	2.30	4.18	7.41	21870

The kinetics of the substitution of pyridine into compounds of Pt (IV) were studied by us in the following reactions:



We also studied the kinetics of the substitution of pyridine into corresponding compounds with the coordinate  $\text{NO}_2 - \text{Pt} - \text{Cl}$ :  $[(\text{NH}_3)_3\text{PtClNO}_2\text{Cl}]Cl$ ,  $[(\text{NH}_3\text{NO}_2)_2\text{PtNO}_2\text{Cl}]$ , and  $[\text{EnNH}_3\text{NO}_2\text{PtClNO}_2\text{Cl}]Cl$ . The end products of the interactions of these compounds were not isolated; however, it is well known [5] that the substitution reaction proceeds only at the  $\text{NO}_2 - \text{Pt} - \text{Cl}$  coordinate. Assuming that the reactions investigated are second order reactions, calculation of the rate constants was carried out by means of the formula for second order reactions. Calculation of the rate constants confirmed that the reactions investigated were bimolecular reactions.

Potentiometric titration of the unreacted pyridine was used to determine the concentrations of the reacting substances.

Reactions of the tetravalent platinum compounds were carried out at 4 temperatures, which permitted calculation of the activation energies of these reactions.

In Table 1 are presented the rate constants and activation energies for the reactions of triammines of tetravalent platinum and of Blomstrand salts. The reactions were carried out at an initial concentration of reactants of 0.03 [mole] liter.

The somewhat differing values of the rate constants for reactions of the compounds  $[(\text{NH}_3)_3\text{ClPtCl}_2\text{Cl}]$ ,  $[\text{En}-\text{PtNH}_3\text{NO}_2\text{Cl}_2\text{Cl}]$ , and  $[(\text{NH}_3\text{NO}_2)_2\text{PtCl}_2]$ , which have the reactive coordinate  $\text{Cl} - \text{Pt} - \text{Cl}$ , is explained by the different substituents located in the other coordinates of these compounds.

From the data presented in the table, it is seen that substitution of chlorine by bromine in the compounds investigated caused almost a three-fold increase in the rate constants in the case of the compounds  $[(\text{NH}_3)_3\text{PtCl}_2\text{BrCl}]Cl$  and  $[(\text{NH}_3\text{NO}_2)_2\text{PtBrCl}]$ , while for the compound  $[\text{EnPtNH}_3\text{NO}_2\text{BrCl}]Cl$  the increase in the rate constant was by a factor of 2.3. During the study of the kinetics of substitution reactions of Pt(II) compounds, we observed almost the same increase in rate constants upon the substitution of chlorine by bromine in Pt(II) monoammines.

TABLE 2

Reaction	25°	30°	35°	40°	E, cal.
	$K \cdot 10^4$ liters/mole/sec.				
	3.0	5.4	9.60	16.7	21180
	7.8	13.5	22.7	37.2	19250
	1.25	2.28	4.10	7.30	21750

Substitution reactions at the  $\text{NO}_2 - \text{Pt} - \text{Cl}$  coordinates in the compounds  $[(\text{NH}_3)_3\text{PtClNO}_2\text{Cl}]Cl$ ,  $[(\text{NH}_3\text{NO}_2)_2\text{PtNO}_2\text{Cl}]$ , and  $[\text{EnPtNH}_3\text{NO}_2\text{NO}_2\text{Cl}]Cl$  proceeded extremely slowly. The values of the rate constants for these compounds were 3 times lower than the values of the rate constants for the corresponding compounds with the reactive coordinates  $\text{Cl} - \text{Pt} - \text{Cl}$ .

To determine the effect of the solvent on the magnitude of the rate constant for the substitution of chlorine by pyridine in the Blomstrand salts  $[(\text{NH}_3\text{NO}_2)_2\text{Cl}_2\text{Pt}]$ ,  $[(\text{NH}_3\text{NO}_2)_2\text{ClBrPt}]$  and  $[(\text{NH}_3\text{NO}_2)_2\text{ClNO}_2\text{Pt}]$ , we carried out these reactions in acetone. The calculated values of the rate constants and activation energies are presented in Table 2.

The data presented in Table 2 show that the value of the rate is almost independent of the substitution of acetone for water.

TABLE 3

Reaction	20°	25°	30°	35°	E <sub>a</sub> , cal.
	K · 10 <sup>4</sup> liters/mole/sec.				
$K \left[ \begin{array}{c} \text{NH}_3 \\   \\ \text{Cl} \end{array} \begin{array}{c} \text{Pt} \\   \\ \text{Cl} \end{array} \begin{array}{c} \text{Cl} \\   \\ \text{Cl} \end{array} \right] + \text{Py}$	36.6	63.0	108.0	180.0	19030
$K \left[ \begin{array}{c} \text{NH}_3 \\   \\ \text{Br} \end{array} \begin{array}{c} \text{Pt} \\   \\ \text{Cl} \end{array} \begin{array}{c} \text{Cl} \\   \\ \text{Cl} \end{array} \right] + \text{Py}$	108.3	176.3	286.0	450.0	17000
$K \left[ \begin{array}{c} \text{NH}_3 \\   \\ \text{NO}_2 \end{array} \begin{array}{c} \text{Pt} \\   \\ \text{Cl} \end{array} \begin{array}{c} \text{Cl} \\   \\ \text{Cl} \end{array} \right] + \text{Py}$	400.0	555.0	752.6	1002.0	10900

\* Values for rate constants K; activation energies E<sub>a</sub> cited in previous work were based on data from preliminary experiments. More accurate data are given here. In the previous work, dimensions of the rate constants K were minutes.

Table 3 is presented to permit comparison of the values of the rate constants for reactions of Pt(IV) with values of the rate constants for reactions of Pt(II).

On comparison of Tables 1 and 3, it is seen that the values of the rate constants for reactions of compounds of Pt(IV) were somewhat less than for reactions of compounds of Pt(II) with the corresponding coordinates. It is impossible to call the comparison absolute and accurate, since the cis substituents were not the same in all compounds.

It follows, then, that substitution reactions of Pt(IV) compounds with  $\text{NO}_2 - \text{Pt} - \text{Cl}$  coordinates are characterized by the lowest rate constants and the highest activation energies, while in the case of Pt(II) monoammines with the same coordinate, substitution reactions are characterized, on the contrary, by the highest rate constants and the lowest activation energies.

I. I. Chernyaev, G. S. Myravelskaya and O. N. Andrianova [5,6] have pointed out the peculiar behavior of the  $\text{NO}_2$  group in the inner sphere of tetravalent platinum.

From the above-cited results, it can be concluded that the study of the kinetics of substitution reactions both of Pt(II) compounds and of Pt(IV) compounds makes possible a quantitative comparison of the trans effect of certain inner sphere substituents. It was shown by this means that the same substituent,  $\text{NO}_2$ , behaves differently in the Pt(II) and Pt(IV) series.

N. S. Kurnakov Institute of  
General and Inorganic Chemistry

Received September 6, 1955

#### LITERATURE CITED

- [1] O. E. Zvyagintsev and E. F. Karandasheva, Proc. Acad. Sci. USSR, 101, 93 (1955).
- [2] A. A. Grinberg, L. E. Nikolskaya and G. A. Shagisultanova, Questions of Kinetics, Catalysis, and Reactivity, 1955, p. 633.
- [3] I. I. Chernyaev, Bull. Inst. Plat., No. 16, 14 (1939).
- [4] A. M. Rubinshtein, Bull. Inst. Plat., Acad. Sci. USSR, No. 13, 21 (1936).
- [5] I. I. Chernyaev and G. S. Muravelskaya, Bull. Inst. Plat., Acad. Sci. USSR, No. 23, 68 (1949).
- [6] I. I. Chernyaev and O. A. Andrianova, Bull. Inst. Plat., Acad. Sci. USSR, No. 23, 24 (1949).

ORGANOBORON COMPOUNDS: SYNTHESIS OF TRIALKYLBORON COMPOUNDS  
FROM ESTERS OF DIBUTYLBORIC ACID

B. M. Mikhailov and T. A. Shchegoleva

(Presented by Academician B. A. Kazansky November 23, 1956)

Trialkylboron compounds are prepared by the action of dialkylzinc [1-3] or Grignard reagents [4-6] on boric acid esters or boron halides. Naturally, these methods permit the preparation only of symmetrical trialkyl compounds of boron. With regard to unsymmetrical compounds in the literature, there is described the preparation of di-n-butylmethylboron by the action of methyl iodide on a metallic derivative of di-n-butylboron which is obtained by the treatment of di-n-butylboron chloride with an alloy of sodium and potassium [7]; however, the physical constants (boiling point) of the substance was not given. Attempts to prepare unsymmetrical boron alkyls by the action of lithium alkyls on dimethylboron bromide did not meet with success owing to the ease with which symmetrization of the initially formed unsymmetrical boron alkyls proceeds [8]. There has also been an unsuccessful attempt to prepare mixed alkylarylboron compounds from an ester of di-n-butylboric acid by reacting it with phenylmagnesium bromide [6].

In the present communication is described the preparation of both symmetrical and unsymmetrical ( $R_2R'B$ ) boron trialkyls by the reaction of the n-butyl ester of di-n-butylboric acid with lithium alkyls. The reaction proceeded, obviously, through the formation of lithium salts of di-n-butylalkylbutoxyborinic acids (I), as may be conjectured by analogy with the reactions of an ester of phenylboric acid and phenyllithium [9].



I

II

$R = C_2H_5; n-C_3H_7; n-C_4H_9$

By the action of hydrogen chloride on solutions of the complex salts, there was formed the corresponding boron trialkyls (II), the isolation of which in the pure form encountered certain difficulties owing to the presence of the ester of di-n-butylboric acid in the reaction products.

Tri-n-butylboron, which differs only slightly in boiling point from the ester of di-n-butylboric acid, was separated from it by treatment, with heating, with a 10% aqueous solution of sodium hydroxide. The ester was saponified by this treatment into the acid which remained in solution during the subsequent dilution, while the tributylboron remained unchanged.

Di-n-butylethylboron and di-n-butylpropylboron were purified by repeated fractional distillation using a small column packed with glass packing. The use of an effective column with a total condenser in the head for the purification did not give positive results.

Under conditions of precise fractionation, symmetrization of the unsymmetrical compounds took place; for example, di-n-butylpropylboron was completely converted by this means into a mixture of tri-n-propylboron and tri-n-butylboron.

EXPERIMENTAL

All the operations were carried out in a nitrogen atmosphere.

Tri-n-butylboron. Butyllithium was prepared from 2.6 g of lithium, 27.4 g of butyl bromide, and 180 ml of ether. An ethereal solution of 27.8 g of the n-butyl ester of di-n-butylboric acid [10] was added to the butyllithium solution, which was cooled to -70°, over the course of 40 minutes; the mixture was stirred at this temperature for another 3 hours and left overnight. On the following day, hydrogen chloride was passed into the reaction mixture until saturation was obtained, the lithium salt was filtered out, and the butyl alcohol was distilled off. The residue was again filtered and distilled under vacuum.

The fraction boiling at 114-119° at 25 mm (22.3 g) was extracted in a separatory funnel with 56 ml of a 10% solution of alkali. After separation of the organic layer (35.6 g), the water and butyl alcohol were distilled from it on a water bath. To the residue, which was an oily material, was added 20 ml of water, whereupon the mixture stratified. The organic layer was separated, dried with benzene, and distilled under vacuum. There was obtained 9.5 g of tributylboron (38% of theory) with a b.p. of 109-110° at 23 mm.

Found %: B 5.94; 5.72  
 $C_{12}H_{27}B$ . Calculated %: B 5.94

Literature data [6]: b.p. 90-91° at 9 mm, 108-110° at 20 mm.

n-Propyl-di-n-butylboron. n-Propyllithium was prepared from 4.65 g of lithium, 27.3 g of n-propyl chloride, and 250 ml of ether. To the solution of propyllithium, which was cooled to -70°, was added over a 2-hour period, an ethereal solution of 50 g of the n-butyl ester of di-n-butylboric acid, the mixture was stirred at this temperature for 2 hours, and left overnight.

The reaction mass was treated in a manner analogous to that described above. The residue was subjected to fractional distillation. The fractions obtained were: 1) 73-76° at 9 mm - 4 g; 2) 76-80° at 9 mm - 21.5 g; 3) 80-95° at 9 mm - 5.3 g; 4) 95-101° at 9 mm - 3.5 g.

The second fraction was n-propyl-di-n-butylboron (yield, 50%), while the fourth fraction was the butyl ester of di-n-butylboric acid. After additional distillation, the n-propyl-di-n-butylboron had a b.p. of 77-79° at 9 mm,  $d_4^{20}$  0.7484.

Found %: B 6.71; 6.66  
 $C_{11}H_{25}B$ . Calculated %: B 6.43

Symmetrization of n-propyl-di-n-butylboron. 26 g of n-propyl-di-n-butylboron having a b.p. of 80-90° at 15 mm was distilled in a column with glass packing (~20 theoretical plates). The external heating temperature was 150-185°. The fractions distilled were: 1) 50.5-54° at 11 mm - 6 ml; 2) 54-95.5° at 11 mm - 7 ml. The first fraction was tri-n-butylboron.

Found %: B 7.98  
 $C_9H_{21}B$ . Calculated %: B 7.71

Literature data [4]: b.p. 62° at 20 mm, 156°.

The residue in the flask was distilled in the usual small, glass packed column. 11 g of tri-n-butylboron, b.p. 96-98° at 12 mm, was obtained.

Found %: B 6.02; 6.04  
 $C_{12}H_{27}B$ . Calculated %: B 5.94

Ethyl-di-n-butylboron. Ethyllithium was prepared from 4.45 g of lithium, 36 g of ethyl bromide, and 250 ml of ether. To the ethyllithium solution, which was cooled to -25°, was added, over a 2.5-hour period, an ethereal solution of 44.8 g of the n-butyl ester of di-n-butylboric acid while the temperature was gradually lowered to -70°. The mixture was stirred at this temperature for 2 hours and left overnight. The reaction mass was treated in a manner analogous to that described above. Upon fractional distillation, these fractions were obtained: 1) up to 67° at 9 mm - 1.1 g; 2) 67-69° at 9 mm - 9.0 g; 3) 69-80° at 9 mm - 4.4 g; 4) 80-94° at 9 mm - 2.3 g; 5) 94-100° at 9 mm - 5.3 g.

The second fraction was ethyl-di-n-butylboron, yield 26%,  $d_4^{20}$  0.7496.

Found %: B 7.06; 7.21  
Calculated %: B 7.02

Analysis of organoboron compounds. To a weighed sample of the material to be analyzed (0.1-0.2 g) was added 1 ml of a 5 N solution of sodium hydroxide and 5 ml of 30% hydrogen peroxide. Vigorous heating (to boiling) of the mixture took place. After violent evolution of gas ceased, another 2 ml of 5 N alkali solution and 3 ml of 30% hydrogen peroxide solution were added. The mixture was refluxed for 20 minutes, 20 ml of 1 N hydrochloric acid was added, and refluxing was continued for another 20 minutes.

After cooling, the excess hydrochloric acid was neutralized with 1 N alkali (methyl orange indicator), mannitol was added, and the mixture was titrated with 0.1 N sodium hydroxide using phenolphthalein indicator.

This method of analyzing organoboron compounds is considerably simpler than the method given in reference [11].

Received November 18, 1955

#### LITERATURE CITED

- [1] E. Frankland and D. Duppa, Ann. Chem. 115, 319 (1860).
- [2] E. Frankland, Ann. Chem. 124, 129 (1862).
- [3] A. Stock and F. Zeidler, Ber. 54, 531 (1921).
- [4] E. Krause and R. Nitsche, Ber. 54, 2784 (1921).
- [5] E. Krause and P. Nobbe, Ber. 64, 2112 (1931).
- [6] J. Johnson, H. Snyder and M. Van Campen, J. Am. Chem. Soc. 60, 115 (1938).
- [7] R. Auten and C. Kraus, J. Am. Chem. Soc., 74, 3398 (1952).
- [8] F. Parsons and D. Ritter, J. Am. Chem. Soc. 76, 1710 (1954).
- [9] B. M. Mikhailov and P. M. Aronovich, Proc. Acad. Sci. USSR, 98, 791 (1954).
- [10] B. M. Mikhailov and T. A. Shchegoleva, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 6, 1124 (1955). (T.p. 1039)\*
- [11] H. Snyder, J. Kuck and J. Johnson, J. Am. Chem. Soc., 60, 110 (1938).

\* (T.p. = C. B. Translation pagination)



## PHOTOCHLORINATION OF DIETHYLDICHLOROSILANE IN THE LIQUID STATE

E. P. Mikheev

(Presented by Academician L. N. Nazarov; December 6, 1955)

The first chlorination of diethyldichlorosilane was carried out with sulfonyl chloride in the presence of benzoyl peroxide by heating the mixture on a water bath for several hours [1,2]. A. D. Petrov and co-workers chlorinated diethyldichlorosilane in the vapor state with gaseous chlorine by irradiation with ultraviolet light [3]. The chlorination was carried out in an apparatus which permitted a considerable portion of the monochloro derivatives formed to escape from the sphere of the chlorination. The duration of the process amounted to 51.5 hours in this case.

We carried out the chlorination of diethyldichlorosilane in the liquid state with gaseous chlorine by irradiation from a 150-watt incandescent lamp. During the photochlorination of diethyldichlorosilane, an induction period, lasting about half an hour under our conditions, was observed at the beginning.\* The chlorination rate, which was practically zero at the beginning, gradually increased during the course of the induction period, and became very high at the conclusion of it. For example, at a chlorine feed rate close to 0.33 mole per hour per mole of compound being chlorinated and at a temperature of 15°, the chlorine was completely reacted, and did not accumulate in the liquid.

It should be noted that, after completion of the induction period, following a brief interruption in the chlorine feed the induction period was absent upon resumption of the chlorination. On the other hand, after a lengthy interruption, upon resumption of the chlorine feed the induction period again set in, the length being greater (within known limits) the longer the interruption.

The cause of the induction period was the presence in the alkylchlorosilanes of dissolved oxygen which, combining with the free radicals formed, hindered the development of the chain process of chlorination as long as it was not completely combined. The sharp inhibiting action of oxygen was observed by us during passage of a slight stream of air simultaneously with the chlorine into the diethyldichlorosilane being chlorinated after completion of the induction period; several seconds after starting the passage of air, the colorless liquid acquired an intense chlorine color which disappeared only several minutes after stopping the flow of air.

The chlorination was stopped upon attaining a weight increase corresponding to the feeding of 1, 0.875, and 0.75 moles of chlorine per mole of diethyldichlorosilane. After chlorination, in addition to the previously described  $\alpha$ - and  $\beta$ -chloroethylidenechlorosilanes, we isolated from the mixture and characterized a dichloro-diethyldichlorosilane, apparently  $\alpha, \beta'$ -dichlorodiethyldichlorosilane. The results of the chlorination are presented in Table 1 (in mole per cent). For the purpose of comparison, results calculated by us from the previously mentioned work [2,3] are presented in the last two columns of the table.

A comparison of the results attests to the indisputable advantage in the use of chlorine over the use of sulfonyl chloride. Comparing the vigorous consumption and rate of chlorination, it must be recognized that liquid-phase chlorination of diethyldichlorosilane is no less efficient than vapor-phase chlorination; moreover, in the first case, the equipment and the carrying out of a liquid phase process is much simpler.

Description of the experiments. The chlorination was carried out in an 800-ml three-necked flask which

\*The induction period was approximately the same length as those observed by us during photochlorination of other alkylchlorosilanes under similar conditions.

TABLE 1

Substance	1 mole of Cl <sub>2</sub>	1 mole of C <sub>2</sub> H <sub>5</sub> Cl	1 mole of C <sub>2</sub> H <sub>5</sub> Cl <sub>2</sub>	δ 15°C	(3)	(2)
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>3</sub>	26	32	40	28	44	
CH <sub>3</sub> CHCl CH <sub>3</sub> CH <sub>3</sub> SiCl <sub>3</sub>	22	21	20	26	11	
ClCH <sub>2</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> SiCl <sub>3</sub>	31	28	27	29	18	
Di- and polychlorides and loss	21	18	13	19	27	

was submerged in a 2-liter Bunsen jar and which was fitted with a 9-bulb reflux condenser, a tube for the introduction of chlorine, and a thermometer. The bulb of the thermometer was placed close to the outlet of the tube carrying the chlorine. For protection from atmospheric moisture, the upper end of the reflux condenser was connected to a calcium chloride tower. The bulb of the incandescent lamp was placed at a distance of 1 to 2 mm from the wall of the Bunsen jar.

700 g of diethyldichlorosilane,  $n_D^{20}$  1.4320 and  $d_4^{20}$  1.0535, was placed in the flask, and then, with irradiation and at room temperature, passage of chlorine into the diethyldichlorosilane at a rate of about 1.5 g/min was begun. All of the liquid in the flask took on the color of chlorine. After 5 minutes, feeding of the chlorine was interrupted, and the reaction mixture was allowed to stand, with irradiation, for 20-30 minutes. At the end of this period, the temperature began to increase, and the liquid gradually decolorized with the liberation of bubbles of hydrogen chloride. An increase in the temperature above 30° was prevented by periodically cooling the flask with water.

After complete decoloration of the liquid, water was circulated in the Bunsen jar, and passage of chlorine was resumed at a rate of 1.5 g/minute, and this was maintained until the desired weight increase was obtained. Cooling with circulating water at a temperature of 3-4° guaranteed maintenance of a temperature of 15-18° in the flask. At the conclusion of the chlorination, the liquid was purged with dry air for 15 minutes to remove the dissolved hydrogen chloride.

Resolution of the mixture was carried out at atmospheric pressure in a column having 30 theoretical plates. Vigorous decomposition of  $\beta$ -chloroethylethyldichlorosilane, mentioned in the literature [3], was observed by us only when using in the column stainless steel packing, which was corroded (it was covered with metal chlorides). The  $\beta$ -chloroethylethyldichlorosilane decomposed rather slowly at its boiling point (182°) on pure stainless steel and also on ceramic packing.

The compositions of the intermediate fractions were computed from the densities. The individual substances were subjected to a second distillation in the column, as a result of which they were obtained in a fairly pure state.

$\alpha$ -Chloroethylethyldichlorosilane, b. p. 163°,  $n_D^{20}$  1.4573,  $d_4^{20}$  1.1985,  $MR_D$  found 43.55, calculated 43.64.

Found %: hydrolyzable Cl 37.02

Calculated %: hydrolyzable Cl 37.01

$\beta$ -Chloroethylethyldichlorosilane, b. p. 182°,  $n_D^{20}$  1.4650,  $d_4^{20}$  1.2166,  $MR_D$  found 43.52, calculated 43.64.

Found %: hydrolyzable Cl 55.17

Calculated %: hydrolyzable Cl 55.52

On heating with anhydrous aluminum chloride,  $\beta$ -chloroethylethyldichlorosilane was rapidly decomposed into ethyltrichlorosilane and ethylene.

Dichlorodioethylethyldichlorosilane. The residues from several experiments, after separation of the monochloroethylethyldichlorosilanes, were subjected to distillation in a wetted-wall column having 10 theoretical plates. The fraction with a b.p. of 212°,  $n_D^{20}$  1.4865,  $d_4^{20}$  1.3412, a colorless liquid, was predominant in the residues. On hydrolysis of this fraction with 0.5 N sodium hydroxide, ethylene was liberated along with other substances  $MR_D$  found 48.42, calculated 48.48.

Found %: hydrolyzable Cl 47.27

For 3 atoms Cl in  $C_4H_8Cl_4Si$  Calculated %: hydrolyzable Cl 47.07

In accordance with the concept of  $\beta$ -cleavage of chloroalkylchlorosilanes, the splitting off of 3 atoms of chlorine and of ethylene during hydrolysis with dilute alkali is characteristic of only one of the six possible isomeric dichlorodiethyldichlorosilanes, for  $\alpha, \beta$  '-dichlorodiethyldichlorosilane.

Appreciation is herewith expressed to A. M. Neshumova for carrying out the determinations of the hydrolyzable chlorine.

Received September 5, 1955

LITERATURE CITED

- [1] D. T. Hurd, J. Am. Chem. Soc., 67, 1813 (1945).
- [2] L. H. Sommer and D. L. Bailey, et al., J. Am. Chem. Soc., 76, 1613 (1954).
- [3] A. D. Petrov, V. A. Ponomarenko et al., Proc. Acad. Sci. USSR, 100, No. 6, 1107 (1955).

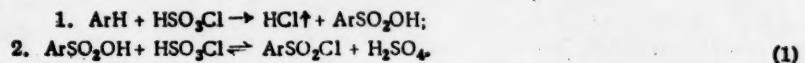


THE QUESTION OF THE MECHANISM OF THE CHLORINATION OF  
ARYLSULFONIC ACIDS WITH CHLOROSULFONIC ACID. CHLORINATION  
OF p-PHENYLURETHYLSULFONIC ACID

V. A. Palm

(Presented by Academician V. N. Kondratyev, October 22, 1955)

It can be considered as established that the chlorosulfonation of aromatic compounds proceeds in two stages [1-5,7]. Of these, the first is practically irreversible, and the second is an equilibrium reaction:



The reversibility of the second stage, which consists of the chlorination of an arylsulfonic acid by chlorosulfonic acid, was demonstrated in the work of A. A. Spryskov and Yu. L. Kuzmina [3,4]\*.

B. Yu. Yasnitsky attempted to study the dependence of the reactivity of substituted benzenes during chlorosulfonation on their structures. However, using rate constants calculated on the assumption of a simple bimolecular process, he was not able to arrive at a true solution to this problem. A quantitative study of the dependence of reactivity on structure can be initiated, in our opinion, only after a detailed study of the mechanism of this type of reaction. Only such a course of investigation, though tedious and requiring great expenditure of work, can yield reliable information for the solution of this problem.

We studied the chlorination of p-phenylurethylsulfonic acid in mixtures of  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_3\text{Cl}$  of different compositions. The same mixtures were used as in the study of the acidity function of the system  $\text{H}_2\text{SO}_4 - \text{HSO}_3\text{Cl}$  [8]. The course of the reaction was followed spectrophotometrically with an SF-4 apparatus. The reaction and compensation cells were thermostated to  $\pm 0.1^\circ$ . Both the forward and reverse reactions were investigated at initial concentrations of p-phenylurethylsulfonic acid (or, respectively, sulfochloride) of the order of 0.01-0.02 mole/liter. The spectrophotometric investigation was carried out at a wave length,  $\lambda$ , of 295  $\mu\text{m}$ .

The kinetic curves obtained obeyed the monomolecular law; this indicated a monomolecular reaction, as would be expected (see Figures 1 and 2). In Figure 1 is shown graphically the attainment of equilibrium from two directions.

The data confirm the observation of A. A. Spryskov and Yu. A. Kuzmina [3,4] that the equilibrium constant for the reaction between the sulfonic acid and its acid chloride depends only to a slight extent on temperature. The equilibrium constant,  $k$ , which was determined in the temperature interval of 20 to  $70^\circ$  at concentrations of  $\text{HSO}_3\text{Cl}$  varying from 4.1 to 24.8 mole %, varied within the limits 3.42-3.83. The average value

$$k = \frac{[\text{sulfochloride}][\text{H}_2\text{SO}_4]}{[\text{sulfonic acid}][\text{HSO}_3\text{Cl}]} = 3.65.$$

The results of the kinetic investigation were treated as in the following example. The experimentally observed pseudomonomolecular rate constant  $\kappa$  is actually a complex quantity:

\*The existence of a true equilibrium is denied by B. Yu. Yasnitsky [6,7]. In our view, this conclusion is somewhat premature.

$$\kappa = k_1 [\text{HSO}_3\text{Cl}] + k_2 [\text{H}_2\text{SO}_4]. \quad (2)$$

where  $k_1$  and  $k_2$  are the bimolecular rate constants for the forward and reverse reactions, respectively, The ratio of  $k_1$  to  $k_2$  is

$$\frac{k_1}{k_2} = K = 3.5. \quad (3)$$

We note that values of  $\kappa$ , determined in one and the same medium for the forward and reverse reactions, agreed satisfactorily.

After the experimental determination of  $\kappa$ , it is possible to determine  $k_1$  and  $k_2$  in each separate case using relationships (2) and (3). In Table 1 are presented values of  $k_1$  obtained by this method in media of different

$\text{HSO}_3\text{Cl}$  contents. The values of the acidity function were determined by us spectrophotometrically using p-nitrochlorobenzene and 2,4-dinitrotoluene as indicators [8]. The values of  $k_1$  in mixtures with  $\text{HSO}_3\text{Cl}$  contents of 95.0 and 97.5 mole % are rough approximations, since it was necessary to measure rates of reactions with half lives of 2.5 to 7 seconds which, with the method used, inevitably led to large percentage errors.

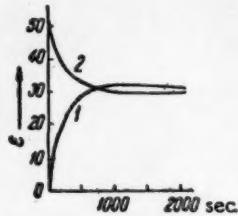
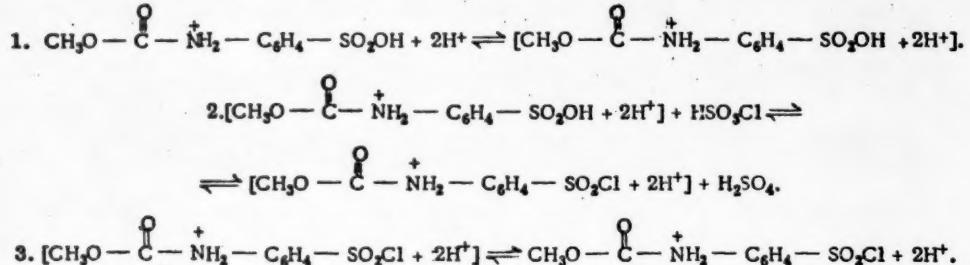


Fig. 1. 1) kinetic curve of the change of absorption coefficient at a wave length of  $295 \text{ M}\mu$  for the chlorination of p-phenylurethylsulfonic acid; 2) the same for the reverse reaction. Concentration of  $\text{HSO}_3\text{Cl}$  24.8 mole %; temperature 41.0°.

2 protons must be added to the p-phenylurethylsulfonic acid. We consider that, owing to the presence of the amino groups, the p-phenylurethylsulfonic acid is no less strongly basic than 2,4,6-trinitroaniline. From this, it is a fair assumption that, in the interval of  $\text{H}_0$  considered, we have to deal with a sulfonic acid which has already completely added one proton. Then, the observed dependence of  $\log k_1$  on  $\text{H}_0$  is explained by the addition of the 2nd and 3rd protons.

The scheme of the investigated reaction can now be written in the following form:



Equilibria 1 and 3 are established instantaneously. The reaction rate is determined by the slow stage 2.

The observed rate constant can be written in the following form:

$$k_1 = \frac{k_1^0}{K_d^n} \gamma h_0^n. \quad (5)$$

TABLE 1

Conc. of HSO <sub>3</sub> Cl mole %	H <sub>0</sub>	Temp. °C	k <sub>1</sub> · 10 <sup>5</sup>	log k <sub>1</sub>	Conc. of HSO <sub>3</sub> Cl	H <sub>0</sub>	Temp. °C	k <sub>1</sub> · 10 <sup>5</sup>	log k <sub>1</sub>
0.0	-10.89	40.0	5.1	4.30*	37.9	-11.61	14.7	12.2	3.92*
		50.1	15.0	3.82*			14.7	16.2	3.79
		57.8	32.3	3.49*			20.1	27.0	3.57
4.1	-10.98	51.0	21.8	3.66	54.6	-11.78	30.3	52.9	3.28
		51.0	20.3	3.69*			11.9	34.7	3.46
		60.1	45.0	3.35			20.0	48.2	3.32
		60.1	46.0	3.34*			20.0	51.8	3.29*
11.1	-11.25	69.5	107	3.97	69.8	-12.06	27.5	124	2.91
		41.0	26.4	3.58*			13.6	123	2.91
		41.0	22.2	3.65			20.0	230	2.64
		50.1	40.7	3.39*			26.5	308	2.51
		50.1	40.7	3.39			3.0	162	2.79
24.8	-11.48	58.0	102	2.99*	81.0	-12.21	7.8	306	2.51
		58.0	86.0	3.07			12.7	433	2.36
		22.5	15.5	3.81			2.7	222	2.65
		30.5	26.0	3.59			8.4	490	2.31
		30.5	27.2	3.57*			2.6	670	2.2
		41.0	51.0	3.29	95.0	-12.43	7.7	1170	1.90
		41.0	53.0	3.28*			2.6	950	2.00
					97.5	-12.56	8.1	1900	1.70

\* The asterisks denote data obtained during the study of the reverse reaction of the conversion of the sulfochloride to sulfonic acid.

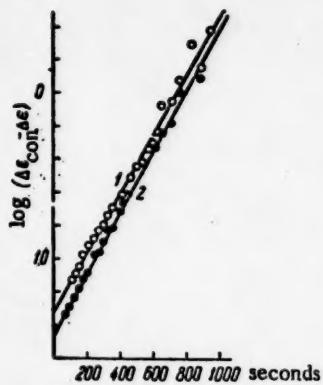


Fig. 2. Kinetic curves, presented in Figure 1, in the coordinates  $\log(\Delta\epsilon_{\text{con}} - \Delta\epsilon)$  and time.

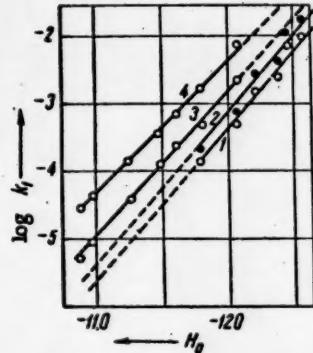


Fig. 3. Dependence of  $\log k_1$  on  $H_0$ . 1) at 3.0°; 2) at 8.0°; 3) at 20.0°; 4) at 35.0°

where  $h_0 = 10 - H_0$ ;  $K_a^*$  is the dissociation constant in water of the complex of p-phenylurethylsulfonic acid with protons when splitting off 2 of the more difficultly added protons;  $k_1^0$  is the true rate constant for Stage 2 of Scheme (4);  $n$  is the index of the degree of dependence of  $k_1$  on the acidity of the medium,  $h_0$ , and is equal to the number of protons added to the sulfonic acid in Stage 1 of Scheme (4);  $\gamma$  is the correction factor for  $h_0^n$ , and depends on the types of charges of the ions of the sulfonic acid participating in Equilibrium 1 of Scheme (4).

The dependence of  $k_1$  on the structure of the sulfonic acid is determined by the constants  $k_1^0$  and  $K_a^*$ . Unfortunately, the method described does not permit calculation of these constants separately. We can calculate  $\gamma$  on the basis of the electrostatic theory of the activity of ions. Taking as a standard a medium with an infinitely large dielectric constant, we obtain:

$$\gamma = -6 \frac{e^2}{2kT\epsilon D} -$$

(6)

The dielectric constant for mixtures of  $H_2SO_4$  and  $HSO_3Cl$  is unknown. As an approximation, a value of 90 can be assumed. The ionic radius can be estimated as  $r = 3\text{A}$ . Then

$$\gamma = e^{-3700/RT}.$$

Knowing  $\gamma$ , the ratio  $K_1^0/K_a^0$  can be calculated. For p-phenylurethylsulfonic acid at  $35.0^\circ$ ,  $K_1^0/K_a^0 = 1.5 \cdot 10^{-24}$ . Calculations at other temperatures are devoid of meaning, since the temperature dependence of  $H_0$  is unknown. The latter can be obtained from a comparison of the results of a study of the dependence of chlorination kinetics on the acidity of the medium for several sulfonic acids.

Sincere appreciation is expressed to N. M. Chirkov for a series of effective counsels and hints in the course of the accomplishment of this work.

Tartu State University

Received October 19, 1955

#### LITERATURE CITED

- [1] L. S. Solodar and Z. N. Shevchenko, *J. Appl. Chem.*, 22, 508 (1949).
- [2] L. S. Solodar and Z. N. Shevchenko, *J. Appl. Chem.*, 22, 874 (1949).
- [3] A. A. Spryskov and Yu. L. Kuzmina, *J. Gen. Chem.*, 21, 714 (1951). (T.p. 787)\*
- [4] A. A. Spryskov and Yu. L. Kuzmina, *J. Gen. Chem.*, 21, 1887 (1951) (T.p. 2097) \*
- [5] B. Yu. Yasnitsky, *J. Gen. Chem.*, 23, 107 (1953). (T.p. 103) \*
- [6] B. Yu. Yasnitsky, *J. Gen. Chem.*, 23, 1953 (1953). (T.p. 2069) \*
- [7] B. Yu. Yasnitsky, *Investigation of the Mechanism of the Reaction of Chlorosulfonic Acid with Certain Aromatic Compounds*, Author's Abstract, Kharkov, 1953.
- [8] V. A. Palm, *Proc. Acad. Sci. USSR*, 108, No. 2 (1956). (T.p. 249) \*

\*T.p. = C. B. translation pagination

## STUDY OF ISOTOPE EXCHANGE BETWEEN GASEOUS OXYGEN AND ALKALI METAL SULFATES AT HIGH TEMPERATURE

Associate Member of the Academy of Sciences, USSR

Vikt. I. Spitsyn and V. G. Finikov

Up to the present time, very little work has been published devoted to the study of isotope exchange between gaseous oxygen and solid oxides and salts of oxygen-containing acids. Allen and Lander [1] studied the exchange of oxygen, enriched with the isotope  $O^{18}$ , with copper, cobalt, and nickel oxides. In the case of  $Co_3O_4$ , the extent of exchange tended toward a limiting value which depended on the temperature (about 36% at 700° and about 67% at 800°). Houghton and Winter [2] studied isotope exchange between gaseous oxygen and  $\gamma$ - $Al_2O_3$ ,  $ThO_2$ ,  $TiO_2$  and  $ZnO$ . The presence of two stages, differing in reaction rate, was established. Studying, with  $O^{18}$  the mechanism of the catalytic oxidation of CO by oxygen in the presence of  $MnO_2$ , S. M. Karpacheva and A. M. Rozen [3] detected isotope exchange between the oxygen of these gases and the catalyst. F. M. Vainshtein and G. Ya. Turovsky [4] explained this phenomenon by the presence of traces of water in the catalyst used. L. Ya. Margolis and E. G. Plyshevskaya [5] showed that the effect of moisture on the rate of exchange of oxygen between  $V_2O_4$  and  $O_2$  is small. L. A. Kasatkina [6] studied the kinetics of isotope exchange of oxygen and water vapor with  $\alpha$ - and  $\beta$ - $MnO_2$  and  $V_2O_5$ , determined the activation energies of the indicated processes, and established the effect on the rate of isotope exchange of such added materials as  $K_2SO_4$  and KOH. The exchange of oxygen between  $O_2$  and  $K_2SO_4$  was not observed at a temperature of 500°. A. V. Trofimov [7] studied the kinetics of exchange between gaseous oxygen and barium, calcium, and sodium carbonates at high temperatures (300-920°). Isotope exchange occurred in all cases, but it affected the crystals of the compounds studied to a limited depth.

Our investigation had as its problem the study of isotope exchange between gaseous oxygen and alkali metal sulfates at high temperatures with the aim of comparing the stability of the oxygen bonds in the indicated salts.

Figure 1 shows the arrangement of the apparatus which was constructed for the experiments. Water, containing about 1.3 atom %  $O^{18}$ , was slightly acidified with  $H_2SO_4$  and subjected to electrolysis. The oxygen obtained was freed from traces of hydrogen in the catalyst tube and dried in traps cooled with a mixture of dry ice and acetone. The rate of movement of gas through the apparatus was regulated automatically. The moving contact rheometer was set at the desired point; upon a fall in the column of mercury, which was used as the rheometric liquid, electrolysis was initiated, replenishing the supply of oxygen in the reservoir cylinder. Electrolysis was automatically discontinued on a drop of the column of mercury in the rheometer tube. The apparatus worked at a pressure 4-5 mm Hg above atmospheric.

The exchange reaction was carried out in a quartz tube heated with an electric furnace. The salt being investigated was placed in a platinum boat inside the tube. In order to reduce the volume of the reaction space a quartz filler was placed in the tube. The temperature was regulated by means of a thermocouple and temperature controller, which was regulated with a potentiometer. Oxygen samples were collected throughout the specified time interval in evacuated receivers, and were analyzed with a series mass spectrometer, type MS-1. The content of  $O^{18}$  in the gas was determined from the ratio of the magnitudes of the peaks at mass 32 and 34 ( $O_2^{16}$  and  $O^{16}O^{18}$ ). Graphs showing the dependence of isotope composition of the effluent gas on time were constructed from the analytical data. This permitted the determination of the amount of  $O^{18}$  entering into the solid phase and, consequently, the extent of exchange. It was preliminarily established that the change in isotope composition of the effluent oxygen owing to exchange with the quartz tube could be neglected up to a temperature of 830°.

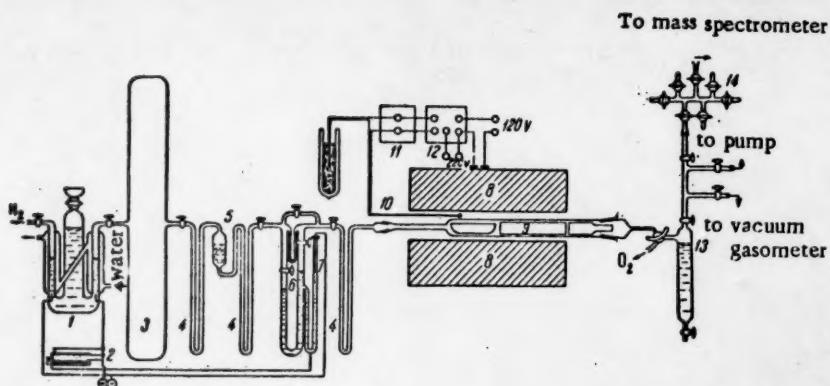


Fig. 1. Flow diagram of the apparatus for the study of isotope exchange between gaseous oxygen and solid salts. 1) electrolytic cell, 2) relay, 3) reservoir cylinder, 4) traps, 5) catalyst tube, 6) rheometer, 7) moving contact, 8) electric furnace, 9) quartz tube with platinum boat, 10) thermocouple, 11) pp potentiometer, 12) temperature controller EPM-47, 13) cylinder for sample collection, 14) gas sample receiver.

TABLE 1

Isotope Exchange Between Gaseous Oxygen and Alkali Metal Sulfates.  
(Time of Exchange, 7 hours)

Compound	$\text{Li}_2\text{SO}_4$			$\text{Na}_2\text{SO}_4$			$\text{K}_2\text{SO}_4$			$\text{Rb}_2\text{SO}_4$			$\text{Cs}_2\text{SO}_4$		
Experiment temp., °C	680	729	775	763	790	818	766	794	821	686	725	752	680	742	787
Exchange in %	1.75	5.74	11.25	0.88	1.46	1.19	0.40	0.73	0.81	1.10	1.60	3.11	0.59	1.32	1.26

Chemically pure preparations of lithium, sodium, and potassium sulfates calcined at a temperature of 500° were used for the exchange. Rubidium and cesium sulfates were prepared from the corresponding nitrates by evaporation with a small excess of  $\text{H}_2\text{SO}_4$  and subsequent calcination to constant weight at a temperature of 700-800°. Analyses for  $\text{SO}_4^{2-}$  content showed that the salts used were of satisfactory purity. Sample size of the compounds studied varied within the limits of 1.1-6.3 g. The maximum temperature of the experiments was different for each sulfate and depended on the volatility of the preparation during its conditioning under high vacuum prior to carrying out the exchange. The decrease in weight after conditioning did not exceed 0.1% of the original value. In Table 1 are presented the results of the experiments, each of which was continued for 7 hours. During this time, 500-600 ml of oxygen (at room temperature and atmospheric pressure) was passed through the reaction space. The decrease in  $\text{O}^{18}$  content was from 0.002 to 0.101 atom %, while the analytical method permitted the determination of a change of  $\pm 0.001$  atom % of  $\text{O}^{18}$ . The average precision of the determination of the extent of exchange in the described experiments was  $\pm 5\%$ , and it decreased to  $\pm 10\%$  when the exchange was less than 0.7%.

The specific surface area of the lithium sulfate was determined by a transient state gas flow method [8], and was  $4.3 \text{ m}^2/\text{g}$ . The specific surface areas of sodium and potassium sulfates, found by the same method, were 1.3 and  $1.6 \text{ m}^2/\text{g}$ , respectively. Comparison of the sizes of crystals under a microscope provided a basis for assuming that the specific surface areas of our samples of rubidium and cesium sulfates differed insignificantly from the specific surface areas of the sodium and potassium sulfates. Therefore, it was possible to assume an average specific surface area of  $1.5 \text{ m}^2/\text{g}$  for the four salts indicated.

In connection with this, that the calculated number of oxygen atoms at the surface of the crystals of the sulfates used is 10-100 times less than the number of atoms undergoing exchange confirms that the exchange proceeded not only at the surface, but also reached the inner regions of the crystals; that is, it accompanied diffusion of  $\text{O}^{18}$  deep into the crystal lattice.

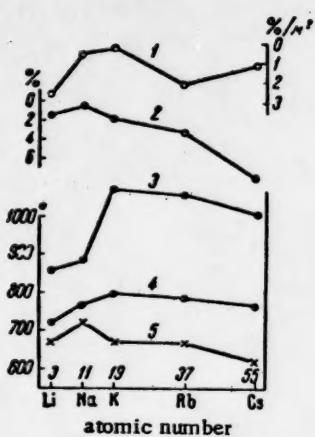


Fig. 2. Comparison of certain physical and chemical properties of alkali metal sulfates. 1) extent of isotope exchange with gaseous oxygen in 7 hours at a temperature of 742-772°, referred to 1 m<sup>2</sup> of surface area of the salt; 2) decrease in weight in 2 hours calcination at 1200°; 3) melting point; 4) temperatures at which reduction of the sulfates by ammonia begins; 5) temperatures at which reduction of the sulfates by hydrogen begins.

That potassium sulfate had the lowest exchange rate in comparison with the other sulfates studied can be connected with its relatively higher stability. An analogous relationship was noted earlier during an investigation of the chemical activity and thermal stability of alkali metal sulfates [9,10]. The curves of Figure 2 were constructed on the basis of our work and the literature data. Many physical and chemical properties of the normal sulfates follow the above-stated rule. The experimental values of the properties studied are characteristic of the middle members of the series: potassium and sodium sulfates.

Direct analysis of the isotopic composition of the oxygen in the sulfates after the exchange experiments was not carried out owing to the difficulty of converting them into compounds suitable for this purpose. We did perform related experiments, studying the isotopic exchange of oxygen with  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{CO}_3$ . The content of  $\text{O}^{18}$  in the solid phase was determined from the data on the change in composition of the gas phase and also from analyses of the oxygen in water after carrying out an exchange between it and the indicated salts. The difference between the figures obtained by the two independent methods was less than 2%, which can be considered as proof of the reliability of the method of calculation used. Over a period of 7 hours, the extent of exchange was 47.3% for  $\text{Na}_2\text{CO}_3$  at 753° and 18.0% for  $\text{Na}_2\text{MoO}_4$  at 574°, which indicates the high mobility of oxygen in the indicated compounds in comparison with the sulfates studied.

The results of the present investigation are in complete agreement with the idea, expressed earlier by one of us [11], of the mutual influence of atoms in alkali salts of oxygen-containing acids. The low stability of lithium sulfate, and, in part, of sodium sulfate can be explained by the development of contrapolarization in the  $\text{SO}_4^{2-}$  anion owing to the appreciable polarizing effect of ions with a relatively small radius —  $\text{Li}^+$  and  $\text{Na}^+$ . The "selective" polarizing action of oxygen in the  $\text{SO}_4^{2-}$  anion with regard to the bulky  $\text{Rb}^+$  and  $\text{Cs}^+$  cations leads to a decrease in stability in the sense of decomposition of rubidium and cesium sulfates into oxides. For the indicated reason, the most stable compound of this series is potassium sulfate. On transition to the molybdate, the greater size of the central atom in the  $\text{MoO}_4^{2-}$  ion, which is constructed similarly to the  $\text{SO}_4^{2-}$  ion, has as its consequence a decrease in the "oneness" of the anion and a weakening of the stability of the bond of the oxygen with it. A similar decrease in the "oneness" of the  $\text{CO}_3^{2-}$  ion occurs owing to the decrease in valence of the central atom. Owing to

If the experimental data in Table 1 on the extent of exchange in the temperature interval 742-772° are placed on a square meter of surface area basis, the following numbers characterizing the relative abilities of the sulfates investigated to exchange with gaseous oxygen are obtained:  $\text{Li}_2\text{SO}_4$ , 2.7;  $\text{Na}_2\text{SO}_4$ , 0.6;  $\text{K}_2\text{SO}_4$ , 0.3;  $\text{Rb}_2\text{SO}_4$ , 2.1;  $\text{Cs}_2\text{SO}_4$ , 0.9. Potassium sulfate had the least ability to exchange with oxygen. The amount of exchange increased on going from potassium sulfate to sodium and lithium sulfates and also on going to rubidium and cesium sulfates.

The anomaly in the dependence of the extent of exchange on temperature observed for  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{Cs}_2\text{SO}_4$  (Table 1) can be connected with the phenomenon of polymorphic transformation which accompanies sintering and, consequently, with the decrease in the specific surface area of the preparation. These questions require additional investigation.

We attempted to make approximate calculations of the activation energy involved in the isotope exchange process. In the case of the three indicated salts, calculations were carried out based on the data from the two lower temperature experiments. The following values (in kcal / mole) were obtained:  $\text{Li}_2\text{SO}_4$ , 39;  $\text{Na}_2\text{SO}_4$ , 54;  $\text{K}_2\text{SO}_4$ , 57;  $\text{Rb}_2\text{SO}_4$ , 40;  $\text{Cs}_2\text{SO}_4$ , 24.

this, sodium carbonate and molybdate undergo thermal dissociation more easily than sodium sulfate.

On the basis of the results presented, it can be surmised that isotope exchange of salts of oxygen-containing acids with gaseous oxygen at high temperatures proceeds more rapidly the less the chemical stability of the corresponding compounds.

The authors express their appreciation of V. V. Filippovsky for assistance in the determinations of the specific surface areas of the sulfates investigated.

Institute of Physical Chemistry  
Academy of Science USSR

Received November 15, 1955

#### LITERATURE CITED

- [1] J. A. Allen and J. Lander, *Nature*, **164**, 142 (1949).
- [2] G. Houghton, E. R. S. Winter, *Nature*, **164**, 1130 (1949); E. R. S. Winter, *J. Chem. Soc.* **1170** (1950); **3342** (1954).
- [3] S. M. Karpacheva and A. M. Rozen, *Proc. Acad. Sci. USSR*, **68**, 1057 (1949); A. M. Rozen and S. M. Karpacheva, *Proc. Acad. Sci. USSR*, **88**, 507 (1953).
- [4] F. M. Vainshtein and G. Ya. Turovsky, *Proc. Acad. Sci. USSR*, **72**, 297 (1950); G. Ya. Turovsky and F. M. Vainshtein, *Proc. Acad. Sci. USSR*, **78**, 1173 (1951).
- [5] L. Ya. Margolis and E. G. Plyshevskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, No. 3, 415 (1952). (T.p. 403)\*
- [6] L. A. Kasatkina, Thesis, D. I. Mendeleev Chemical-Technological Inst., 1953.
- [7] A. V. Trofimov, *Proc. Acad. Sci. USSR*, **96**, 335 (1954).
- [8] G. Kraus and J. W. Ross, *J. Phys. Chem.* **57**, 334 (1953).
- [9] Ya. A. Fialkov and S. D. Shargorodsky, *Notes of the Inst. of Chemistry*, **7**, 415 (1940).
- [10] Vikt. I. Spitsyn and V. I. Shostak, *J. Gen. Chem.* **19**, 1801 (1949) (T.p. a-251) • Vikt. I. Spitsyn and M. A. Meerov, *J. Gen. Chem.*, **22**, 2079 (1952). (T.p. 2133) •
- [11] Vikt. I. Spitsyn, *J. Gen. Chem.*, **17**, 11 (1947); **20**, 550 (1950).

\*T.p. = C. B. translation pagination

## KINETICS OF THE SPONTANEOUS DECOMPOSITION OF POTASSIUM OZONIDE

Associate Member of the Academy of Sciences, USSR, I. A. Kazarnovsky,

S. I. Raikhshstein and L. N. Bykova

In 1949-1951, a new class of oxides was discovered in our laboratory — the ozonides of the alkali metals, which are red crystalline materials having the structure  $M^+O_3^-$  with the previously unknown molecular ion of ozone  $O_3^-$  [1,2]. As magnetic measurements showed, this ion possesses the characteristics of a free radical with one unsaturated valence [1]\*.

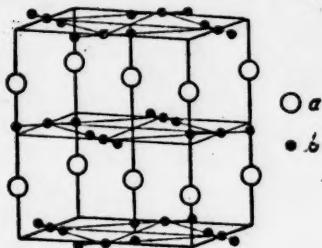


Fig. 1. Crystal lattice of potassium ozonide. a) potassium ions; b)  $O_3^-$  ions.

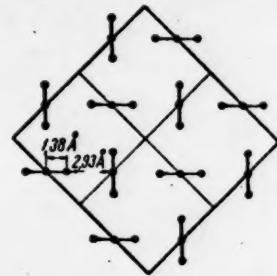
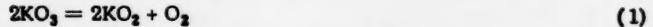


Fig. 2. Surface network of  $O_3^-$  in the potassium ozonide lattice.

X-ray investigation of potassium ozonide [3] disclosed a tetragonal lattice of the potassium bifluoride type, similar to the potassium azide lattice [4] and with the same unit cell parameters\*\* (see Figure 1).

The analogy of these two structures indicates that the  $O_3^-$  ion, just as the  $N_3^-$  ion, has a linear form [1]. The electronic structure of the  $O_3^-$  ion can be represented approximately by the formula  $\ddot{O}-\dot{O}-\ddot{O}$ . The distance between two neighboring oxygen atoms in the  $O_3^-$  ion is about 1.38 Å [1]. In the potassium ozonide lattice,  $O_3^-$  ions form an endless surface network in which the distance between the closest atoms of two neighboring  $O_3^-$  ions is 2.93 Å (see Figure 2).

A characteristic of the alkali metal ozonides is their instability at room temperature and their slow decomposition into peroxides and oxygen, for example, according to the equation



The basic thermodynamic values of this reaction are  $\Delta H_{298}^0 = -11.6$  kcal.;  $\Delta S_{298}^0 = 33$  cal/degree;  $\Delta F_{298}^0 = -21.6$  kcal. [6]. Hence, the dissociation pressure of potassium ozonide at 298° K is  $p_{O_2} = 10^{16}$  atm. The dissociation of potassium ozonide into potassium peroxide and oxygen is, consequently, an irreversible reaction.

The present work comprises an investigation of the kinetics of the spontaneous decomposition of potassium ozonide. Studying the reaction was of interest, since it proceeds, although slowly, at an entirely measurable rate both at room temperature and at temperatures below zero.

\* In 1951, Whaley and Kleinberg repeated our investigation of potassium ozonide and confirmed our results [5].

\*\* Within the limits of 0.01 Å.

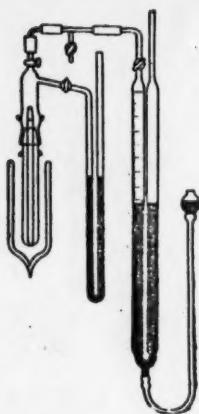


Fig. 3. Apparatus for measuring the decomposition rate of potassium ozonide.

the average decomposition rate in the induction period was 0.23% per hour, and, in the active period, the rate reached 2.3%  $KO_3$  per hour, i. e., it increased by a factor of 10; at  $-9^\circ$ , these rates were 0.03 and 1.5% per day, i. e., it increased by a factor of 50.

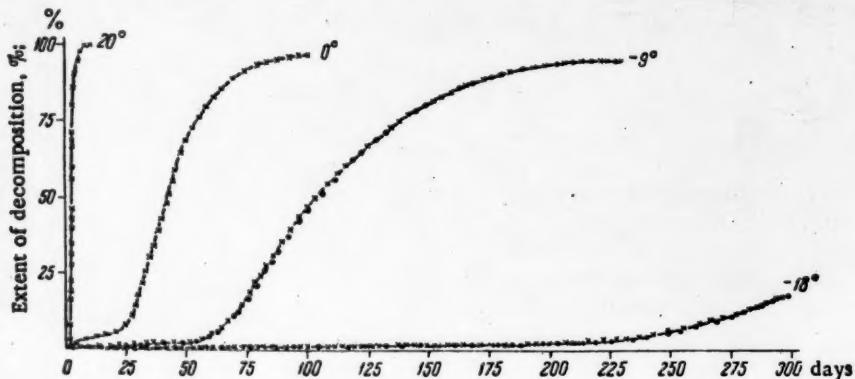


Fig. 4. Kinetics of the decomposition of potassium ozonide.

The half-life period was 2 hours at  $50^\circ$ , 3.5 days at  $+20^\circ$ , 41 days at  $0^\circ$ , and 103 days at  $-9^\circ$ . Practically complete decomposition was attained in 4 hours at  $50^\circ$ , in 10 days at  $+20^\circ$ , in 101 days at  $0^\circ$ , and in 230 days at  $-9^\circ$ . In the induction period at  $-18^\circ$ , which lasted 205 days, less than 1%  $KO_3$  was decomposed, which corresponds to a loss of active oxygen of about 0.2%. After 8 months, the oxygen loss was about 1%, while the active oxygen content of the original preparation was 42.6%.

It is interesting to note the good reproducibility of the kinetic measurements in spite of the extreme slowness with which the reaction proceeded. As an example, we present some results at  $-9$  and  $-18^\circ$  (see Table 1).

Calculation of the activation energy,  $E$ , using the Arrhenius equation gave, for those portions of the active

\*In view of the extreme sensitivity of potassium ozonide to moisture, all operations with this preparation were carried out in a "dry" cell.

TABLE 1

Expt. No.	Temp., °C	Length of induction period, days	Half-life, days
7	-9	54	103.5
8	-9	55	103.0
11	-18	205	-
12	-18	203	-

Calculation of the activation energy,  $E$ , using the Arrhenius equation gave, for those portions of the active period having a constant rate, the following values:

$t, ^\circ\text{C}$	50-20	20-0	0-(-18)
$E, \text{kcal.}$	23.4	22.9	21.6

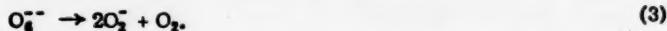
As is well known, the question of the induction period and the activated state is not clear at present. In order to arrive at a mechanism for the reaction studied, one can propose a hypothesis based on the

defect crystal structure theory [7]. We assume that a gradual accumulation of defects in the crystal lattice of the decomposing potassium ozonide takes place during the induction period, and the active state is characterized by the attainment of a certain critical limit at which decomposition begins in the phase saturated with defects and in the new  $\text{KO}_2$  phase. From this moment, the reaction proceeds at the phase boundaries, and its rate at first increases and then decreases in accordance with the change in the size of the boundaries.

Starting with the crystalline structure of potassium ozonide, it can be assumed that, with sufficient amplitude of the thermal vibrations, neighboring  $\text{O}_3^-$  ions form intermediate complexes with partial or complete saturation of the free valencies, for example, according to the scheme:



These complexes, accumulating during the induction period, decomposed then into  $\text{O}_2^-$  ions and molecular oxygen according to:



As a consequence of the saturation of the free valencies of the  $\text{O}_3^-$  ions during the proposed formation of intermediate complexes, the latter must be diamagnetic, while both  $\text{KO}_3$  and  $\text{KO}_2$  are paramagnetic. It is possible that magnetic measurements could shed light on the mechanism of the investigated reaction.

We have started magnetic susceptibility measurements on the products of the decomposition of potassium ozonide in various stages of this process.

L. Ya. Karpov Physico-chemical  
Research Institute

Received January 10, 1956

#### LITERATURE CITED

- [1] I. A. Kazarnovsky, G. P. Nikolsky and T. A. Abletsova, Proc. Acad. Sci. USSR, 64, 69 (1949).
- [2] G. P. Nikolsky, Z. A. Bagdasaryan and I. A. Kazarnovsky, Proc. Acad. Sci. USSR, 74, 69 (1951).
- [3] G. S. Zhdanov and Z. V. Zvonkova, J. Phys. Chem., 25, 100 (1951).
- [4] S. Hendricks, L. Pauling, J. Am. Chem. Soc., 47, 2908 (1925).
- [5] Th. P. Whaley, J. Kleinberg, J. Am. Chem. Soc., 73, 79 (1951).
- [6] G. P. Nikolsky, L. I. Kazarnovskaya, Z. A. Bagdasaryan and I. A. Kazarnovsky, Proc. Acad. Sci. USSR, 72, 713 (1950).
- [7] J. S. Anderson, Annual Reports Progress Chem., 43, 104 (1947); A. L. Rees, Chemistry of the Defect Solid State, London, 1954.



## POLYMORPHISM OF RUBIDIUM AND CESIUM NITRATES AND THEIR INTERACTION WITH BARIUM NITRATE

V. E. Plyushchev, I. B. Markina and L. P. Shklover

(Presented by Academician G. G. Urazov, December 24, 1955)

The polymorphic transformations of rubidium and cesium nitrates have caught the attention of a series of investigators, both for the sake of the transformations themselves and in connection with the study of certain systems of which these compounds form a part.

Four different modifications of rubidium nitrate have been established in the temperature range from room temperature to the melting point. One of the transition points corresponds to a temperature of 164.4° according to Bridgeman [1], 164° (cooling) and 166° (heating) according to A. P. Rostkovsky [2], and 160.5° according to N. Pushin and M. Radoichich [3]. A second transition point was found at 216° (cooling) by N. Pushin and M. Radoichich [3] and at 222° (cooling) and 229° (heating) by A. P. Rastkovsky. A high-temperature modification of rubidium nitrate, which exists above 290–292°, was first established by A. P. Rostkovsky [2]. Cesium nitrate has two modifications with a transition point at 156° (cooling) and 161° (heating) according to Gossner [4], at 153.7° according to Bridgeman [1], and at 151.5° according to N. Pushin and M. Radoichich [3].



Fig. 1. Heating curves. 1)  $\text{RbNO}_3$ ; 2)  $\text{CsNO}_3$

The majority of the investigators did not report any analytical data which would establish the purity of the compounds at their disposal. Bridgeman [1] working with preparations destined for the determination of the atomic weights of the elements, noted that impurities lower the transition temperature from one modification into another.

There is some variation in the melting point data reported for rubidium and cesium nitrates. For example, the melting point of rubidium nitrate has been reported as 306° [5], 313° [6], 312° [3,7], and 316° [2], and for cesium nitrate 414° [8], 408° [5], and 417.5° [3] have been reported.

In the present work, an investigation was undertaken of the polymorphism of rubidium and cesium nitrates and of the binary systems which they form with barium nitrate, the investigation being carried out by the method of thermal analysis (by means of heating curves recorded differentially using the pyrometer system of N. S. Kurnakov and platinum/platinum-rhodium thermocouples calibrated at the standard calibration points).

These two systems have not been studied up to the present; it is assumed that they belong to a simple eutectic type [9].

The original nitrates were thoroughly pure compounds. Their content of impurities consisting of other alkali metals, as determined by spectral analysis, is given by the following figures (in weight%). Found for  $\text{RbNO}_3$ :

Li<0.02, Na<0.03, K<0.04, Cs<0.0035; Found for  $\text{CsNO}_3$ : Li<0.02, Na<0.03, K<0.015, Rb<0.045.

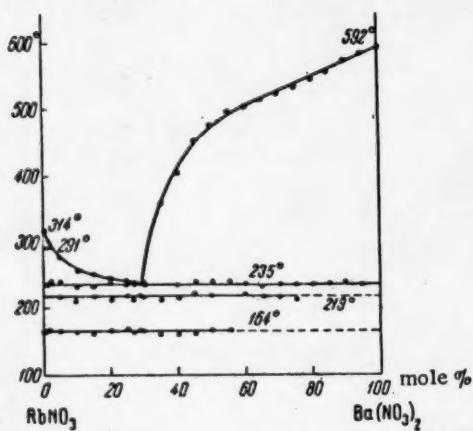


Fig. 2. Melting point diagram for the system  $\text{RbNO}_3$  -  $-\text{Ba}(\text{NO}_3)_2$ .

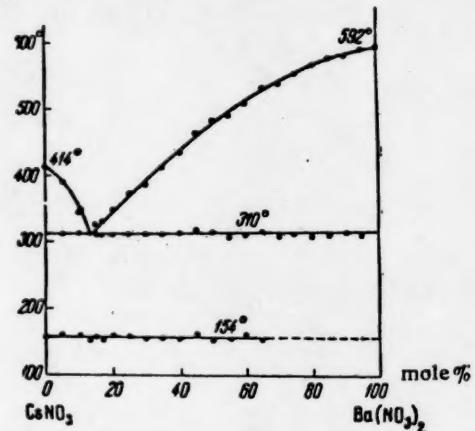


Fig. 3. Melting point diagram for the system  $\text{CsNO}_3$  -  $-\text{Ba}(\text{NO}_3)_2$ .

During the recording of the heating curves of the pure rubidium and cesium nitrates (5-6 g sample weights), different heating rates, from 6 to 14 degrees/minute, were tested. In Figure 1 are presented the heating curves of rubidium and cesium nitrates (7.6 degrees/minute heating rate), in which the maximum temperatures correspond to melting and the remainder to transition points of the different modifications. These transitions are enantiotropic.

Thus, the following characteristic points were found for  $\text{RbNO}_3$ : 164° ( $\delta \rightarrow \gamma$ ), 219° ( $\gamma \rightarrow \beta$ ), 291° ( $\beta \rightarrow \alpha$ ) and 314° (m.p.); for  $\text{CsNO}_3$ : 154° ( $\beta \rightarrow \alpha$ ) and 414° (m.p.).

TABLE 1  
The System  $\text{RbNO}_3$  -  $\text{Ba}(\text{NO}_3)_2$

RbNO <sub>3</sub> , mole %	Polymorphic transformation $\text{RbNO}_3$			Eutectic	Polymorphic transformation of $\text{RbNO}_3$	Melting point	RbNO <sub>3</sub> , mole %	Polymorphic transformation $\text{RbNO}_3$			Eutectic	Polymorphic transformation	Melting point
	$\delta - \gamma$	$\gamma - \beta$	—					$\delta - \gamma$	$\gamma - \beta$	—			
100	164	219	—		291	314	55	166	222	239	—	—	452
99	162	217	235		291	299	50	164	220	240	—	—	473
98	167	217	240		290	295	45	167	221	234	—	—	494
95	162	219	240		—	275	40	—	222	235	—	—	502
90	162	212	230		—	253	35	—	217	230	—	—	512
85	160	217	231		—	250	30	—	218	237	—	—	520
80	164	214	237		—	244	25	—	214	234	—	—	530
75	170	221	234		—	240	20	—	—	233	—	—	543
73	163	214	235		—	238	15	—	—	232	—	—	554
71	164	219	235		—	235	10	—	—	237	—	—	573
70	164	216	235		—	240	5	—	—	234	—	—	581
65	158	213	239		—	355	0	—	—	—	—	—	592
60	150	219	235		—	402							

Samples weighing 6-7 g were used in the study of the systems  $\text{RbNO}_3$  -  $\text{Ba}(\text{NO}_3)_2$  and  $\text{CsNO}_3$  -  $\text{Ba}(\text{NO}_3)_2$ , and samples were prepared with intervals of 5% change in composition; the eutectic points were found graphically and confirmed experimentally. As in all of the prior investigations, we did not establish a polymorphic

transformation for barium nitrate.

The results are presented in Tables 1 and 2 and in Figures 2 and 3.

TABLE 2  
The System  $\text{CsNO}_3 - \text{Ba}(\text{NO}_3)_2$

$\text{CsNO}_3$ , mole %	Polymorphic transformation	Eutectic Temperature, °C	Melting point	$\text{CsNO}_3$ , mole %	Polymorphic transformation	Eutectic Temperature, °C	Melting point
100	154	—	414	50	150	312	480
95	158	310	388	45	151	305	488
90	154	311	345	40	157	307	507
87	150	310	310	35	149	313	530
85	154	310	326	30	—	305	535
83	155	310	331	25	—	308	550
80	157	310	348	20	—	305	563
75	157	311	370	15	—	306	575
70	154	310	385	10	—	310	580
65	152	310	412	5	—	305	587
60	152	312	435	0	—	—	592
55	160	317	463				

The character of the crystallization of the melts and the presence of eutectic breaks in the heating curves, corresponding to high concentrations of the original components of the systems studied, do not provide a basis for a conclusion that solid solutions are formed in the systems. It can be considered as established that the system  $\text{RbNO}_3 - \text{Ba}(\text{NO}_3)_2$  is of the eutectic type with polymorphic transformations of one of the components above and below the eutectic temperature; the system  $\text{CsNO}_3 - \text{Ba}(\text{NO}_3)_2$  is also of the eutectic type with a polymorphic transformation of one of its components below the eutectic temperature. The eutectic point of the first system corresponds to 71 mole %  $\text{RbNO}_3$  and 235°, and that of the second system to 87 mole %  $\text{CsNO}_3$  and 310°.

M. V. Lomonosov Moscow  
Institute of Fine Chemical Technology

Received December 23, 1955

#### LITERATURE CITED

- [1] P. W. Bridgman, Proc. Am. Acad., 51, 590 (1915-1916).
- [2] A. P. Rostkovsky, J. Russ. Phys. Chem. Soc., 62, 2067 (1930).
- [3] N. Pushin and M. Radoichich, Z. anorg. allg. Chem., 233, 41 (1937).
- [4] B. Gossner, Z. Kryst., 38, 142 (1904).
- [5] F. M. Jaeger, Z. anorg. allg. Chem., 101, 193 (1917).
- [6] F. L. Haigh, J. Am. Soc., 34, 1144 (1912).
- [7] O. H. Wagner, Z. phys. Chem., 131, 409 (1928).
- [8] T. W. Richards, E. H. Archibald, Z. anorg. Chem., 34, 353 (1903).
- [9] S. D. Gromakov and L. M. Gromakova, J. Phys. Chem. 27, 1545 (1953).



THE REACTION OF UNSYMMETRICAL ORGANIC  $\alpha$ -OXIDES WITH ACETONE  
IN THE PRESENCE OF BORON FLUORIDE

F. G. Ponomarev

(Presented by Academician I. N. Nazarov, December 22, 1955)

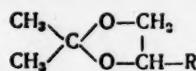
There has been practically no study of the condensation of  $\alpha$ -oxides of the type  $\text{CH}_3-\text{CH}-\text{R}$  with acetone



in the presence of boron fluoride catalyst. The literature reports only the reaction with epichlorohydrin, the methyl ether of glycide [1], and propylene oxide [2].

In the development of our previous investigations [3], it was of interest to prepare a series of cyclic ketals not described in the literature, and to trace the influence of substituents attached to the oxide ring on the reaction of  $\alpha$ -oxides with acetone under the influence of boron fluoride catalyst.

We investigated the condensation of acetone with glycide, its ethers (ethyl, isopropyl, n-butyl, isoamyl, and benzyl), and with styrene and butadiene oxides. These experiments showed that the indicated  $\alpha$ -oxides react with acetone with the formation of the corresponding cyclic ketals:



$\text{R} = \text{CH}_2\text{OAlk, CH}_2\text{OCH}_2\text{C}_n\text{H}_n, \text{CH}_2\text{OH, C}_6\text{H}_5, \text{CH} = \text{CH}_2$ .

It was shown that substituents in the  $\alpha$ -oxide molecule greatly increase its reactivity. For example, if the substituted olefin oxides studied by us react with acetone to form ketals in yields of 30-63%, then, under identical conditions, the total yield of ketals from ethylene oxide comprises 12% [1]. Butadiene oxide gave the ketal (VIII) with a yield of 26%.

Styrene oxide formed the ketal (VII) in 47% yield. Glycide, similarly to its methyl ether [1] under identical conditions, gave the ketal (VI) in 30% yield.

A comparison amongst the reactivities of glycide ethers with acetone shows that the reactivity increases with an increase in molecular weight, as evidenced by the following yield figures: ethyl ether, 44% of a ketal (I); isopropyl ether, 47% of a ketal (II); isobutyl ether [3], 47.5% of a ketal; n-butyl ether, 49% of a ketal (III); and isoamyl ether, 63.3% of a ketal (IV).

It is possible that the effect on ketal yield in the homologous series of glycide ethers is connected with a decrease in their tendency toward polymerization. In support of this, it may be pointed out that the formation of ketal (IV) usually proceeds without a heat effect, but the formation of ketals (I) and (II) is accompanied by a vigorous evolution of heat.

The  $\alpha$ -oxides used were prepared from the chlorohydrins of glycerin [4], butadiene [5], and styrene. The latter was prepared by means of monochlorourea.

Condensation of  $\alpha$ -oxides with acetone. The experiments were carried out according to the following

method. To a 5-fold amount of acetone in a flask was added  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  catalyst in an amount of 0.5% of the total reactants, and the oxide was then introduced in small portions. If heat was evolved, the mixture was cooled so that the temperature of the reaction mixture did not exceed 30°. After standing for a day, the mixture was washed with a concentrated potash solution, dried with potash, the acetone distilled off, and the condensation product distilled under vacuum or at atmospheric pressure.

TABLE 1

Substance	B.p. at 10 mm	$d_{4}^{20}$	$n_D^{20}$	MR <sub>D</sub>		Mol. wt., cryoscopic	
				Found	Calc.	Found	Calc.
I	49-50	0.9606	1.4164	41.10	40.88	159.2	160.2
II	56-57	0.9441	1.4168	46.39	46.47	177.6	174.3
III	72-73	0.9797	1.4380	51.21	51.10	185.7	188.2
IV	81-82	0.9305	1.4260	55.69	55.73	201.8	202.3
V	59-60	1.1270	1.5340	60.85	61.24	219.8	222.3
VI	70-71	1.0755	1.4338	32.00	32.51	134.6	132.2
VII	95-96	1.1101	1.5273	50.98	50.42	178.8	178.3
VIII	121-123 (760 mm)	0.9200	1.4189	35.17	35.14	123.4	128.2

With glycide and the oxides of styrene and butadiene, the experiments were carried out in the following manner. The mixture of acetone and  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  was cooled to -5°, the oxide, also cooled to -5°, was added, and the mixture allowed to stand in ice water for 2 hours and at room temperature for a day. The reaction products were then separated and treated as previously described.

Separate experiments showed that, during condensation with acetone without cooling, styrene oxide polymerized vigorously, and practically no dioxolan (VII) was isolated. It was also noted that the yield of ketal (VI) decreased from 30 to 19% in experiments at room temperature. The use of benzene as a solvent in the condensation  $\alpha$ -oxides with acetone, as established in the case of glycide and its isopropyl ether, did not eliminate the simultaneous occurrence of polymerization of the oxides, and, therefore, did not lead to an increase in ketal yields. The formulas and basic physicochemical constants for all of the cyclic ketals prepared are given in Table 1. In the case of substance (VI), a hydroxyl number determination gave, in %: found, OH 12.60; calculated for  $\text{C}_6\text{H}_{12}\text{O}_3$ , OH 12.78.

The cyclic ketals are colorless, mobile liquids with an agreeable odor. They are readily soluble in alcohol and ether and difficultly soluble in water. They are stable with respect to alkalies and unstable with respect to acids.

The structures of all ketals (I-VIII) were demonstrated by hydrolysis with dilute (5%) sulfuric acid; upon agitation with the acid, they saponified to the original acetone and the corresponding hydrolytic products. For example, from 2,2-dimethyl-3-phenyldioxolan (VII) was obtained acetone (b.p. 56-57°, acetone oxime m.p. 60°) and the expected phenyl glycol. The latter was in the form of snow-white leaflets with a m.p. of 65-67°. A m.p. of 67-68° is reported in the literature for this phenyl glycol [6].

#### LITERATURE CITED

- [1] A. A. Petrov, *J. Gen. Chem.*, **10**, 981 (1940).
- [2] A. A. Petrov, *J. Gen. Chem.*, **16**, 61 (1946).
- [3] F. G. Ponomarev, L. N. Cherkasova and R. M. Chernysheva, *J. Gen. Chem.*, **25**, 1753 (1955) (T.p. 1705).\*
- [4] F. G. Ponomarev, *Reports of the Voronezh State Univ.*, **17**, 113 (1950); *J. Gen. Chem.*, **20**, 2064 (1950), (T.p. 2135);\* *J. Gen. Chem.*, **22**, 929 (1952) (T.p. 985); *Reports of the Voronezh State Univ.*, **32**, 3 (1953).
- [5] A. A. Petrov, *J. Gen. Chem.*, **8**, 131 (1938); *Reports of the Voronezh State Univ.*, **10**, 101 (1938).
- [6] Beilstein, V. 6, 907.

\* T.p. = C. B. Translation pagination.

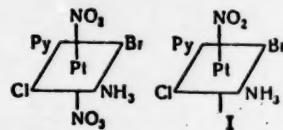


THE PREPARATION OF COMPLEX COMPOUNDS OF TETRAVALENT PLATINUM  
WITH FIVE AND SIX DIFFERENT SUBSTITUENTS IN TRANS- AND CIS-  
CONFIGURATIONS

L. N. Essen and A. D. Gelman

(Presented by Academician A. N. Frumkin, December 12, 1955)

We have previously reported [1] the preparation of complex compounds of tetravalent platinum with six different substituents in the inner sphere having the composition and structure:

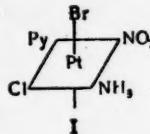


The synthesis of these compounds was based on the rule of I. L. Chernyaev [2] and, particularly, on the concept of increased trans-effect of the nitro group in tetravalent platinum compounds. However, later on over the course of several years, we were unable to carry out the synthesis of other isomers of the same composition on the basis of these same principles.

The absence of reactions resulting in the substitution of addenda in the trans-position to the nitro group in Pt(IV) compounds has been observed by a number of investigators, and has been explained by the extremely high trans-effect of the nitro group [3,5].

Our failure with the synthesis of isomers and also a detailed review of the earlier work of other authors has forced us to the conjecture that the nitro group, which has a considerable trans-effect in divalent platinum compounds, does not exert such an effect in Pt(IV) compounds. An analogous proposal was stated by G. B. Boky and S. S. Batsanov [6] on the basis of measurements of coordinate refractions.

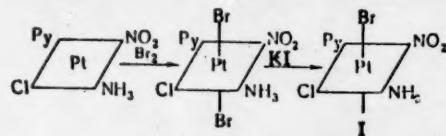
Rejection of the universally accepted concept of the increased trans-effect in tetravalent platinum compounds has opened up a new route for the synthesis of isomeric heterosubstituted tetravalent platinum compounds. Thus, for the isomer



the following synthesis route was conceived.

A complex divalent platinum compound,  $[\text{PyNH}_3\text{ClNO}_2\text{Pt}]$ , served as the starting material. Oxidation of this compound with bromine would be expected to yield the tetravalent platinum dibromide  $[\text{PyNH}_3\text{ClNO}_2\text{Br}_2\text{Pt}]$ , in which, according to our conjecture, the most reactive coordinate is  $\text{Br}-\text{Pt}-\text{Br}$  and not, as would be assumed, the coordinate  $\text{NO}_2-\text{Pt}-\text{Cl}$ . Therefore, by the action on the tetravalent platinum dibromide of KI in the amount

required for the substitution of one atom of bromine by iodine, the desired trans-isomer should be obtained:



We prepared the initial nitrochloride  $[\text{PyNH}_3\text{ClNO}_2\text{Pt}]$  by the action of the calculated amount of sodium nitrite on  $[\text{PyNH}_3\text{Cl}_2\text{Pt}]$ , in contrast to the prior method - cocrystallization of  $[\text{PyNH}_3\text{Cl}_2\text{Pt}]$  and  $[\text{PyNH}_3(\text{NO}_2)_2\text{Pt}]$  [2]. Oxidation with bromine was carried out at room temperature.

The bromine was added drop-wise to a suspension of  $[\text{PyNH}_3\text{ClNO}_2\text{Pt}]$  in water, and the reaction mixture was carefully stirred. With the addition of the first drops of bromine, the original material became greenish brown, and then, as more bromine was added, the color of the material changed to bright yellow. The bright yellow suspension was filtered, well washed with cold water, and dried. The dry material was analyzed for platinum, halogens, and nitrogen.

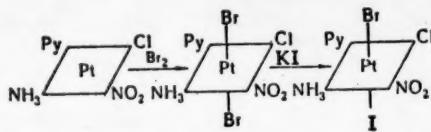
Found %: Pt 36.30; 36.99;  $\Sigma \text{Cl} + 2\text{Br}$  36.24; N 7.59; 8.16  $[\text{PyNH}_3\text{ClNO}_2\text{Br}_2\text{Pt}]$ . Calculated %: Pt 36.66;  $\Sigma \text{Cl} + 2\text{Br}$  36.68; N 7.89; Mol. wt. 532.5

In view of the poor solubility of  $[\text{PyNH}_3\text{ClNO}_2\text{Br}_2\text{Pt}]$  in water, the latter reaction in the course of the preparation of  $[\text{PyNH}_3\text{ClNO}_2\text{BrI}\text{Pt}]$ , that is, the substitution of iodine for one atom of bromine, had to be carried out by the action of potassium iodide on a suspension of  $[\text{PyNH}_3\text{ClNO}_2\text{Br}_2\text{Pt}]$  and not on a solution. The reacting materials were heated on a water bath for 20-25 minutes. Upon the addition of the KI, the material immediately became dark brown. As a result of heating and careful trituration, the isolated inclusions of unreacted, bright yellow starting material disappeared. After cooling, the dark brown suspension was filtered, washed with water, and then recrystallized from hot alcohol. Analysis of the product obtained gave the following results:

Found %: Pt 33.59; 33.33;  $\Sigma \text{Cl} + \text{Br} + \text{I}$  41.85; 41.55; N 6.66; 6.41  $[\text{PyNH}_3\text{ClNO}_2\text{BrI}\text{Pt}]$ . Calculated %: Pt 33.68;  $\Sigma \text{Cl} + \text{Br} + \text{I}$  41.81; N 7.24; Mol. wt. 579.5

The configuration of the thus obtained isomer was confirmed both by the method of preparation and by reduction to the divalent platinum compound  $[\text{PyNH}_3\text{BrI}\text{Pt}]$ .

For the synthesis of the cis-isomer  $[\text{PyNO}_2\text{NH}_3\text{ClBrI}\text{Pt}]$ , using as a starting material the complex nitrochloride  $[\text{PyNO}_2\text{NH}_3\text{Cl}\text{Pt}]$  with the cis-configuration, we followed the route already described in the preceding synthesis, i.e., oxidation of  $[\text{PyNO}_2\text{NH}_3\text{Cl}\text{Pt}]$  with bromine and then substitution of one of the bromines by iodine:



Bromine was added drop-wise, with good agitation, to an aqueous suspension of  $[\text{PyNO}_2\text{NH}_3\text{Cl}\text{Pt}]$ . The colorless starting material became bright yellow. Analysis of the well-washed and dried product gave:

Found %: Pt 36.43; 36.48;  $\Sigma \text{Cl} + 2\text{Br}$  37.25; N 8.03  $[\text{PyNO}_2\text{NH}_3\text{ClBr}_2\text{Pt}]$ . Calculated %: Pt 36.66;  $\Sigma \text{Cl} + 2\text{Br}$  36.68; N 7.89; mol. wt. 532.5.

The compound prepared, having a composition identical with the above-described  $[\text{PyNH}_3\text{ClNO}_2\text{Br}_2\text{Pt}]$ , was distinguished from it by its properties (see Table 1); that is, the two compounds were isomers.

With the presence in the  $[\text{PyNO}_2\text{NH}_3\text{ClBr}_2\text{Pt}]$  of only one active coordinate (Br-Pt-Br), the substitution of bromine by iodine proceeded smoothly.

An aqueous suspension of  $[\text{PyNO}_2\text{NH}_3\text{ClBr}_2\text{Pt}]$  was heated on a plate and acted on by precisely the calculated

TABLE 1

Outward appearance	Finely crystalline material, bright yellow color	Finely crystalline material, bright yellow color	Dark brown needles	Finely crystalline material, brown color
Index of refraction*	$N_g = 1.868$ $N_p = 1.835$	$N_g = 1.920$ $N_p = 1.780$ Material darkened above 180°	$N = 1.910$ 207	$N_g = 1.920$ $N_p = 1.788$ 232
M.P., °C	237	0.02	0.059	233
Solubility in water at 25°. g/100 g of solution				Opalescence at room temperature
Electrical conductivity at 25°. ***			10 000 13.9 μ ohm <sup>-1</sup> cm <sup>2</sup>	10 000 57.8 71.4
v liter/ mole			Opalescence on heating	10 000 128.9
Behavior toward AgNO <sub>3</sub>				
Behavior toward NH <sub>4</sub> OH				Dissolved

\* Isomer prepared previously by us [1].

\*\* Determined by E. E. Burow.

\*\*\* Electrical conductivity was determined 30 minutes after solution began.

amount of potassium iodide. The color of the material gradually changed from bright yellow to light brown. Heating was continued for about 5 minutes, and then the reactants were slowly cooled to room temperature.

The product, recrystallized from hot alcohol, was a finely crystalline, light brown material. Analysis of this material gave (in %):

Pt 33.75; 33.65;  $\Sigma$  Cl + Br + I 41.55; 41.20; N 7.09; 7.57

which data agree well with theory.

The *cis*-configuration of the [PyNO<sub>2</sub>NH<sub>3</sub>ClBrIPt] was confirmed both by the method of preparation and by reduction to the divalent platinum compound [PyNO<sub>2</sub>NH<sub>3</sub>ClPt].

Properties of the compounds prepared are presented in Table 1. They indicate that three compounds of the composition [PyNH<sub>3</sub>ClBrINO<sub>2</sub>Pt], one of which was previously prepared by us [1], are stereoisomers. Their synthesis confirms the correctness of our conjecture that the trans-effect of the nitro group in tetravalent platinum compounds is insignificant.

Institute of Physical Chemistry  
Academy of Sciences, USSR

Received December 12, 1955

#### LITERATURE CITED

- [1] A. D. Gelman and L. N. Essen, Proc. Acad. Sci. USSR, 75, No. 5, 693 (1950).
- [2] I. I. Chernyaev, Bull. Inst. Plat., No. 4, 243 (1926).
- [3] I. I. Chernyaev and A. N. Fedorova, Bull. Inst. Plat., No. 7, 73 (1929); No. 8, 73 (1931).
- [4] I. I. Chernyaev and G. S. Muraveiskaya, Bull. Inst. Plat., No. 23, 39 (1949); No. 25, 35 (1950).
- [5] G. S. Muraveiskaya, Candidate's dissertation, 1954.
- [6] G. B. Boky and S. S. Batsanov, Proc. Acad. Sci. USSR, 95, No. 6, 1205 (1954).

THE REDUCTION OF SELENIUM DIOXIDE, DISSOLVED IN SULFURIC ACID,  
BY SULFUR DIOXIDE

A. G. Amelin and E. V. Yashke

(Presented by Academician S. I. Volkovich, August 17, 1955)

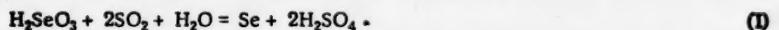
The reduction of selenium dioxide, dissolved in sulfuric acid, by sulfur dioxide is frequently encountered in commercial practice. However, this process has been insufficiently studied.

It is well known that, during the action of sulfur dioxide on solutions of selenium dioxide in 10-40% sulfuric acid, the sulfur dioxide completely precipitates the selenium from solution [1]. The rate of the reduction increases with a decrease in the concentration of the sulfuric acid and with an increase in temperature [2]. In concentrated sulfuric acid, selenium dioxide is not reduced by sulfur dioxide; moreover, metallic selenium dissolves in such acid, and solution is more intensive the higher the temperature [3,4].

In the present work, the process of the reduction of selenium dioxide dissolved in 60-85% sulfuric acid was studied.

The rate of reduction of selenium dioxide dissolved in more concentrated acid decreases to a very small value having no practical significance.

The reduction of selenium dioxide dissolved in sulfuric acid can be represented as follows:



This reaction is bimolecular, and its rate is given by a second order equation; the water has no effect on the order of the reaction, since the change in the concentration of water is insignificantly small.

$$\frac{dc}{dt} = kcb, \quad (1)$$

where c is the concentration of selenium dioxide in the solution (g/liter), b is the concentration of  $\text{SO}_2$  in the solution (g/liter), and k is the reaction rate constant ( $\text{seconds}^{-1}$ ).

During treatment of the solution by passage through it of a continuous stream of sulfur dioxide or of a gas mixture containing sulfur dioxide (as is usually done), the value of b is constant, and, consequently, the rate of Reaction (1) is determined by a first order equation.

Integrating Equation (1) and solving for kb, we obtain

$$kb = \frac{1}{\tau} \log \frac{c_0}{c} . \quad (2)$$

in which  $c_0$  is the initial concentration of selenium dioxide and c is the concentration at time  $\tau$  (g/liter).

Description of the laboratory experiments. The laboratory apparatus, in which were carried out the experiments confirming the correctness of the selection of Equation (2) as characterizing the rate of the process under consideration, is shown in Figure 1. It consisted of a constant temperature water bath, 1, fitted with a stirrer, 2, a toluene temperature controller, 3, and an electric heater, 4, which was connected through a relay. The diffuser, 5, which was made of molybdenum glass, was placed in the constant temperature bath.

10-11 ml of sulfuric acid containing a known amount of dissolved selenium dioxide was introduced into each apparatus.

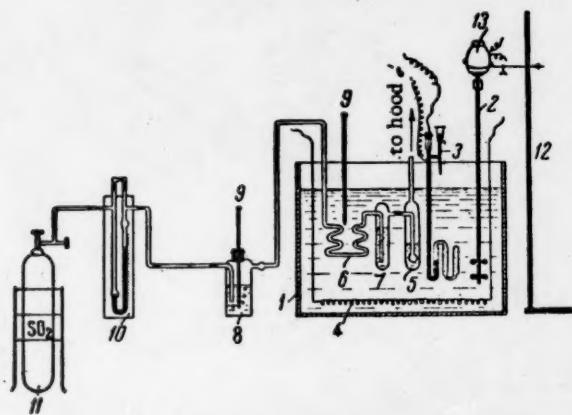


Fig. 1. Diagram of apparatus for the study of conditions for precipitation of selenium from solutions of selenium dioxide in sulfuric acid. 1—constant temperature bath, 2—stirrer, 3—temperature controller, 4—electric heater, 5—main diffuser, 6—preheater coil, 7—pretreater, 8—Drechsel gas washing bottle with water, 9—thermometer, 10—theometer, 11—SO<sub>2</sub> cylinder, 12—stand, 13—electric motor.

With a constant temperature in the water bath, 100% sulfur dioxide, preheated to the temperature of the experiment in the glass coil, 6, which was submerged in the bath, was passed through the solution. Depending on the requirements of the experiment, the sulfur dioxide was passed through the solution for from 15 to 600 minutes.

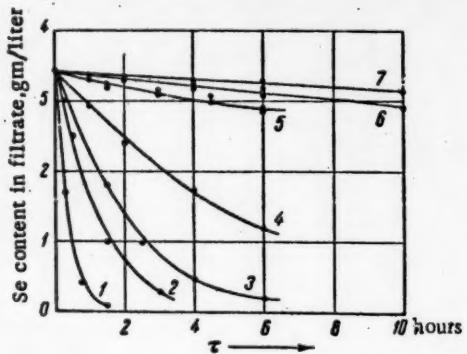


Fig. 2. Variation in selenium dioxide content of the sulfuric acid with duration of treatment with sulfur dioxide and with concentration of sulfuric acid at 50°. 1—60.17% H<sub>2</sub>SO<sub>4</sub>, 2—65.6% H<sub>2</sub>SO<sub>4</sub>, 3—67.8% H<sub>2</sub>SO<sub>4</sub>, 4—70.1% H<sub>2</sub>SO<sub>4</sub>, 5—75.58% H<sub>2</sub>SO<sub>4</sub>, 6—79.8% H<sub>2</sub>SO<sub>4</sub>, 7—85.0% H<sub>2</sub>SO<sub>4</sub>.

In order to maintain constant acid concentration throughout the course of all experiments, pretreater, 7, in which the gas stream was saturated with water vapor, was introduced into the system. The amount of acid in the pretreater was 22 ml, and the acid concentration was the same as in the main apparatus. In order to maintain constant acid concentration in the pretreater, the sulfur dioxide was humidified in a Drechsel gas washing bottle, 8, containing water and inserted in the system before the preheater. The temperature of the

water in the Drechsel bottle was maintained at a level such that the amount of water vapor removed from the Drechsel bottle compensated for the water lost by vaporization from the acid in the pretreater.

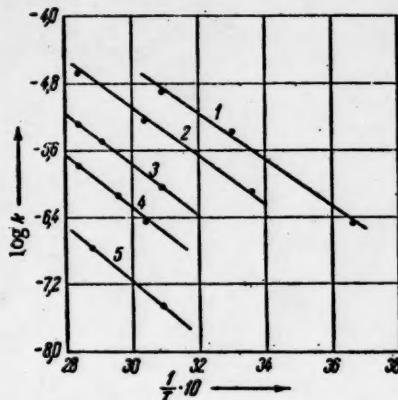


Fig. 3

Fig. 3. Variation in reaction rate constant with temperature. 1) 60.13%  $\text{H}_2\text{SO}_4$ , 2) 64.15%  $\text{H}_2\text{SO}_4$ , 3) 70.1%  $\text{H}_2\text{SO}_4$ , 4) 74.1%  $\text{H}_2\text{SO}_4$ , 5) 85.0%  $\text{H}_2\text{SO}_4$ .

Fig. 4. Values of the activation energy and  $z_0$  for the reduction by sulfur dioxide of selenium dioxide dissolved in 60-85% sulfuric acid.

The experiments were carried out in the following manner. After the required temperature had been attained in the bath, sulfur dioxide was passed through the acid being investigated. At the conclusion of the experiment, the flow of sulfur dioxide was stopped, and  $\text{SO}_2$  was purged from the apparatus by passing air through it at a rate of 0.5-0.75 liter/minute. The apparatus was not removed from the bath during purging, and this contributed to faster removal of the sulfur dioxide from the acid. After purging, the acid in the apparatus was diluted to 15%  $\text{H}_2\text{SO}_4$ , and the solution was filtered through filter paper. After the filtration, the volume of the filtrate (including the water from washing the residue in the filter) was measured, and 25 ml of this solution was analyzed for selenium content by the Marvin method. Knowing the initial selenium content of the solution prior to the analysis and the content in the filtrate after the analysis, we were able to determine the amount of selenium dioxide reduced.

The results of the experiments, which were carried out at temperatures of 0-80°, were plotted separately for each temperature (at intervals of 10-15°), and a series of curves for the various concentrations of sulfuric acid were obtained on each graph. The graph for a temperature of 50° is shown in Figure 2.

The results obtained for the dependence of  $c$  on  $\tau$  were worked up by Equation (2). The thus obtained values of the reaction rate constant for five sulfuric acid concentrations are presented in Figure 3. From the slopes of the lines and the positions of the individual points on them were obtained values of the activation energy,  $E$ , and the constant,  $z_0$ , in the equation:

$$k = z_0 e^{-E/RT}$$

In Figure 4 are presented the data obtained in this manner.

As already mentioned above, the experiments were carried out using 100% sulfur dioxide for the reduction of the selenium dioxide dissolved in acid. However, in industry the interest is in reduction with less concentrated gas.

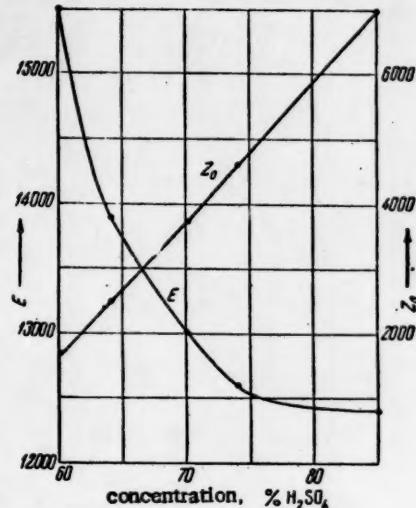


Fig. 4

For the treatment of a solution of selenium dioxide in sulfuric acid with a gas mixture of any  $\text{SO}_2$  content, the reaction rate will be given by Equation (2), in which  $b$  represents the solubility of  $\text{SO}_2$  in the sulfuric acid under the given conditions. This was confirmed by experiments on the reduction of selenium dioxide, dissolved in 61.0% sulfuric acid, with a gas mixture of different  $\text{SO}_2$  content.

Received August 5, 1955

#### LITERATURE CITED

- [1] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, 1933. (Trans.).
- [2] A. G. Amelin and Z. B. Borodastova, *Chem. Ind.*, No. 5, (1945).
- [3] I. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 10, 748 (1930).
- [4] J. Milbauer, *Chem. Obzor*, 14, No. 6, 105 (1939).

## INVESTIGATION OF THE RESIN FROM THE ROOTS OF FERULA GUMOSA BOISS

G. V. Pigulevsky and T. N. Naugolnaya

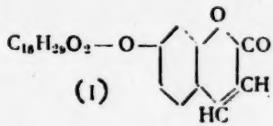
(Presented by Academician A. L. Kursanov, February 6, 1956)

The products of the secretory activity of the roots of *Ferula gumosa* Boiss (*F. galbaniflua* Boiss, et Buchs.) have not been studied until recently. The so-called "galbanum" resin has been obtained from the secretions which are formed on the stalks and inflorescences as brown, drop-like formations [1].

Approaching the investigation of the root resin, we expected to find materials characteristic of "galbanum" resin. Different samples of "galbanum" were first studied by the Russian investigator Hirschsohn [2]. Investigating one of the samples, which had been supplied from Iran, Hirschsohn isolated an acid which he called galbanic acid. He did not give its melting point, and indicated only that it was soluble in alkalies.

Tschirch and Knitl [3-5] determined the melting point of the acid, which Hirschsohn had supplied, and carried out an elemental analysis. The analysis corresponded to the formulas  $C_{18}H_{22}O_2$  and  $C_{20}H_{30}O_3$ .

Recent investigators have not confirmed the presence of galbanic acid. The presence of the galbano-resinotannol ester of umbelliferone (I) has been established



which, on heating with sulfuric acid, forms up to 20% free umbelliferone and alcohol-resinotannol  $C_{18}H_{30}O_3$ . The structure of the indicated resinotannol was not elucidated.

That the results of Hirschsohn could not be duplicated was due, apparently, to the fact that the origin of the galbanic resin at his disposal was different from that of the resin used by other investigators. The roots of *F. gumosa*, which served as material for our investigation, were collected in the Ashkhabad region (Central Asia). The resin, which was isolated from the roots by extraction with acetone, was purified from undesirable contaminants by treatment with chloroform and then with ether.

The residue after the elimination of the ether was a thick, tacky, transparent, brown material. The yield of resin was 22.7%. Properties of the resin: acid number, 58; ester number, 139.2; OH, 3.54%. The resin gave a reaction with azulene. It was soluble in alcohol, ether, chloroform, and benzene.

A crystalline acid, for which we reserve the name galbanic acid, was isolated from the resin by treatment with alkali. The m. p. of the acid was 92-93°. The acid rotates the plane of polarized light,  $[\alpha]_D - 35.2^\circ$  (in alcohol).

Analysis of the acid permitted assignment of the formula  $C_{24}H_{30}O_5$ . The acid had lactone properties. It gave a silver salt having the composition  $C_{27}H_{29}O_3COOAg$ . The methyl ester,  $C_{23}H_{29}O_3COOCH_3$ , is a liquid. The ethyl ester,  $C_{25}H_{29}O_3COOC_2H_5$ , had a melting point of 81-82°;  $[\alpha]_D - 37.7^\circ$  (in chloroform). The addition of 4 molecules of hydrogen during hydrogenation in the presence of Pt catalyst indicates the presence

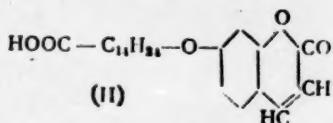
in the molecule of galbanic acid of four hydrogenatable double bonds.

Octahydrogalbanic acid,  $C_{24}H_{38}O_5$ , was obtained in the form of an uncrystallizable, vitreous material. Rotation  $\alpha$  of the acid  $[\alpha]_D^{22} -44.6^\circ$ . The lactone ring of the octahydro acid was less stable than that of the original acid,  $C_{21}H_{30}O_5$ .

Too high a value was obtained in the determination of the acid number; \*\* this is explainable by opening of the lactone ring.

On dehydrogenation with selenium, on a level with other products not studied by us, was obtained a crystalline substance with a m. p. of 229.5-230.5° and the composition  $C_9H_6O_3$ , which did not give a melting point depression with umbelliferone and which possessed characteristic properties of the latter compound. Galbanic acid can be considered as a derivative of coumarin. Raman and ultra-violet spectra confirm this supposition. The absorption spectrum of galbanic acid is very close to the absorption spectrum of umbelliferone.

A conjectural structure for galbanic acid, which exhibits optical activity, can be represented as (II):



## EXPERIMENTAL

Taking into account the acid nature of the resin, it was separated into acid and neutral portions by treatment of an ethereal solution of the resin with 5% potassium hydroxide.

The alkaline extract was heated to eliminate traces of ether. After cooling, it was diluted with 50% sulfuric acid. The precipitate was extracted by heating with a low-boiling gasoline. On cooling, a colorless crystalline material, m.p. 92-93°, precipitated.

Found %: C 72.08; 72.21; H 8.05; 8.32.  $C_{24}H_{30}O_5$ . Calculated %: C 72.33; H 7.59

The molecular weight by the Rast method was 409, calculated for  $C_{24}H_{30}O_5$ , 398.

Acid number: found 130, 130.6, 140.5; calculated for  $C_{23}H_{29}O_3COOH$ , 141.0.

Hydroxyl groups were determined by the method of Chugaev-Tserevitinov.

Found %: OH 3.92; 4.13.  $C_{23}H_{29}O_3$ COOH. Calculated %: OH 4.26

The silver salt was prepared by double decomposition of the potassium salt of the acid, m. p. 92-93°, with an aqueous solution of  $\text{AgNO}_3$ .

Found %: Ag 22.10; 21.90.  $C_{23}H_{29}O_3COOAg$ . Calculated %: Ag 21.35

The acid exhibited lactone properties. On heating with an excess of alkali, part of the latter was consumed in splitting the lactone ring with the formation of the corresponding salt. The acid was liberated unchanged by acidification of the solution. This explains the ester number of the investigated acid.

Ester number, found: 143.38; 149.86.  $C_{24}H_{30}O_5$ . Ester number, calculated: 141.0

Raman spectra of the acid melting at 92-93° were determined in chloroform solution (30%).  $\Delta\nu$ : 136(3); 458(3); 983(1); 1098(4); 1155(8); 1197(8); 1231(4); 1350(4); 1553(10); 1611(10); 1713-1726(1).

Absorption spectra were determined in the ultra violet region,  $c = 0.00535$  mole/liter (ethyl alcohol);

\* The acid possesses an anomalous rotatory dispersion  $\alpha_V/\alpha_I$  1.05;  $\alpha_I/\alpha_J$  0.55.

\* \* Ester No. was probably meant [Translator].

bands of maximum absorption for galbanic acid are (A): 3240-3260; 2520; for umbelliferone: 3260-3270; 2500-2520; 2430-2440.

Preparation of the ethyl ester  $C_{23}H_{29}O_3COOC_2H_5$ . The ethyl ester was prepared in the usual manner by heating on a water bath for 1 hour with a 4% solution of sulfuric acid in ethyl alcohol. After dilution, the product was extracted with ether. The ethereal solution was washed with a 1 N solution of soda, then with water, and dried. After elimination of the ether, slow crystallization in the form of acicular nodules began. More rapid crystallization resulted from dilution with ethyl alcohol. The m. p. of the ester was 81-82°. The ethyl ester can be prepared in the cold by allowing the acid to stand in a solution of ethyl alcohol containing 3-6% HCl. The yield of ester was 95%. Saponification of the ester is reversible and yields the acid melting at 92-93°.

Found %: C 73.30; 73.21; 73.34; H 8.14; 8.06; 8.08.  $C_{23}H_{29}O_3COOC_2H_5$ . Calculated %: C 73.21; H 8.04

Molecular weight by the Rast method: found, 392; calculated for  $C_{23}H_{29}O_3COOC_2H_5$ , 426.

Ester number: found, 271.63, 269.54; calculated, 263.1°.

Hydrogenation of the acid melting at 92-93°. The hydrogenation was carried out in ethyl alcohol solution in the presence of platinum black. The sample weight was 1 g. The catalyst was Pt.

The presence of four double bonds required 224 ml  $H_2$  (0°, 760 mm). The hydrogenation was carried out over a period of 16 hours. After elimination of the alcohol, the hydrogenation product was extracted with ether and dried. The ether was eliminated from the ethereal solution. A vitreous, uncrystallizable material remained.

Found %: C 70.61; 70.58; H 9.75; 9.62.  $C_{24}H_{33}O_5$ . Calculated %: C 70.90; H 9.42

Acid number: found 189.64, 192.57.

Botanical Institute of the Academy of Sciences  
of the USSR

Received October 28, 1955

#### LITERATURE CITED

- [1] A. A. Fedorov and N. P. Kiryalov, Raw Material from Plants, 1, Bot. Inst. Acad. Sci. USSR Press, 1950, p. 143.
- [2] E. Hirschsohn, Pharm. Zs. f. Russland, 225 (1875); 32, 353 (1893); Chem. Zeitung., 195 (1899).
- [3] A. Tschirch and A. Knitl, Arch. der Pharm., 237 (1899).
- [4] A. Tschirch and K. Kuylenstjern, Arch. der Pharm., 535 (1904).
- [5] A. Tschirch and E. Stock, Die Harze, 2, 1. Hälften, 1935.

\* The calculation was made taking into account the presence of a lactone ring.



## ALKALOIDS OF THE SIBERIAN MOONSEED (MENISPERMUM DAURICUM)

T. N. Ilyinskaya

(Presented by Academician A. L. Kursanov, February 6, 1956)

The Siberian moonseed (*Menispermum dauricum*), of the moonseed family (*Menispermaceae*) is a perennial herbaceous plant, widely distributed in Eastern Siberia and in the Far East. Kondo and Narita isolated from the Siberian moonseed (*Menispermum dauricum*) the alkaloid dauricine, a yellow amorphous substance of the composition  $C_{38}H_{44}N_2O_6$  with a melting point of 115°;  $[\alpha]_D - 139^\circ$  (in alcohol). More recently, these same authors isolated from the Siberian moonseed [*Menispermum dauricum*] the alkaloid tetrandrine, a crystalline substance of the composition  $C_{38}H_{42}N_2O_6$  with a melting point of 217°;  $[\alpha]_D + 263.1^\circ$  (in chloroform).

In 1950, the Far Eastern Expedition of the All-Union Research Institute of Medicinal and Aromatic Plants (A. I. Shreter) collected the above-ground portion and the rhizome of Siberian moonseed [*Menispermum dauricum*]; analysis showed that all the organs of this plant contain alkaloids.

Plants, in the fruit-bearing phase, collected in the Far East in 1954 (N. A. Melnikov) were investigated. The alkaloids were isolated separately from the above-ground portions and from the rhizome and roots.

The alkaloids were extracted from the raw material with dichloroethane in ammoniacal medium. The alkaloids were extracted from the dichloroethane extract with 10% sulfuric acid, the acid solution of alkaloids was alkalinized with ammonia while cooling, and the alkaloids were again extracted with dichloroethane, then with acid, and finally with chloroform. The chloroform solution of alkaloids was dehydrated with anhydrous sodium sulfate, filtered, the solvent distilled off to dryness, and the alkaloids dried at 50-60°. By the above-described treatment, a total of 166 g of alkaloids was obtained from the herb; the yield of alkaloids was 0.3%.

The total alkaloids from the above-ground portion of Siberian moonseed [*Menispermum dauricum*] were a brown powder, readily soluble in chloroform and alcohol, sparingly soluble in ether and ethyl acetate, and almost insoluble in water. After repeated recrystallization of the total alkaloids from ethyl ether, an individual alkaloid, crystallizing as needles assembled into star clusters, was obtained. The alkaloid melted at a temperature of 161-162°.

0.2000 g substance, 20 ml alcohol,  $l$  1.9 dm;  $\alpha - 1.5^\circ$ ;  $[\alpha]_D - 78.9^\circ$ .  
0.4652 g substance, 18.6 ml alcohol,  $l$  1.9 dm;  $\alpha - 3.75^\circ$ ;  $[\alpha]_D - 78.9^\circ$ .

Upon recrystallization from ethanol, the alkaloid melted at 181-182°. The alkaloid was readily soluble in chloroform, methanol, butanol, and alkaline solutions, moderately soluble in benzene and ethyl ether, sparingly soluble in water, and did not dissolve in petroleum ether. The alkaloids isolated by us differed in properties from those previously isolated from Siberian moonseed [*Menispermum dauricum*], dauricine and tetrandrine, and constitute a new base from this plant.

The composition of the alkaloid was established by ultimate analysis:

Found %: C 67.11; 66.99; H 7.14; 6.98; N 4.02; 4.16. Calculated %: C 67.50; H 7.10; N 4.09

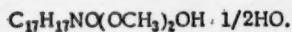
Hydroxyl groups, by Tserevitinov's method, were:

Found %: OH 8.01; 8.33 Calculated %: OH 7.54

Methoxy groups, by Fibek's method, were:

Found %:  $\text{OCH}_3$  17.44; 17.80. Calculated %:  $\text{OCH}_3$  17.10

Thus, this alkaloid, isolated from Siberian moonseed [Menispermum dauricum], has the composition  $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N} \cdot 1/2\text{H}_2\text{O}$  and contains 2 methoxy and 1 hydroxyl groups; whence, its structural formula is:



A number of derivatives of the alkaloid were prepared, and their melting points were determined.

The composition and the physicochemical constants of the alkaloid and its derivatives provide a basis for the assertion that the alkaloid isolated by us is identical to the alkaloid sinomenine isolated from the East Asiatic plant Sinomenium acutum [3,4], which does not grow in the Soviet Union.

In Table 1 are presented the physicochemical constants of our alkaloid and of sinomenine.

TABLE 1

	Alkaloid from Siberian Moonseed [Menispermum dauricum]	Sinomenine
Empirical formula	$\text{C}_{19}\text{H}_{24}\text{O}_4\text{N} \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{C}_{19}\text{H}_{23}\text{O}_4\text{N}$
Mol. wt.	Found 349.5; Calculated 338	329
Melting point	161-162° (from ether) 181-182° (from alcohol) -78.9° (in alcohol) 229-231°	163 and 181°
$[\alpha]_D$	-82.0° (in water)	-78.9° (in alcohol)
Hydrochloride m. p.	229-231°	231°
$[\alpha]_D$	232-233°	233°
Hydrobromide m. p.	214-218°	215° (with decomp.)
Nitrate m. p.	180-184° (with decomp.)	-
Sulfate m. p.	216-217°	-
Perchlorate m. p.	159-162°	~140°
Picrate m. p.	94-95°	-
Picrolonate m. p.	175-177°	-
Chloraurate		

In addition to sinomenine, a base was isolated from the herb moonseed in a small quantity with a m. p. of 227-229°,  $[\alpha] - 120^\circ$  (in pyridine), and the alkaloid dauricine was isolated from the roots and rhizome of moonseed.

All-Union Research Institute of  
Medicinal Plants

Received September 29, 1955

#### LITERATURE CITED

- [1] H. Kondo and S. Narita, Chem. Zentr., 2, 264 (1927).
- [2] H. Kondo and S. Narita, J. Pharm. Soc. Japan, 49, 103 (1929).
- [3] H. Kondo, E. Ochiai and T. Nakajima, Chem. Zentr., 3, 1167 (1923).
- [4] N. Ischiwari and Chugai-Iji-Shipo, 959, 991 (1920). (Cited in [3]).

## STRUCTURAL DIAGRAM OF THE SYSTEM TITANIUM-IRON

I. I. Kornilov and N. G. Boriskina

(Presented by Academician I. P. Bardiny, January 18, 1956)

A series of works [1,2] has been devoted to a consideration of the questions of the chemical interaction of titanium with other elements of the periodic system. The structural diagram of the system titanium-iron from the titanium side has been studied by many authors [3-5]. In this system from the titanium side, the authors have detected a eutectic corresponding to the composition 32% Fe at a temperature of 1060-1085°, and the metallic compound  $TiFe$  (54% Fe) having a space-centered cubic lattice with the parameter 2.982 Å.

At 15-17.5% Fe and 585-600°, the  $\beta$ -solid solution of titanium decomposed eutectoidally into  $\alpha+TiFe$ . The presence of the compound  $Ti_2Fe$ , detected by certain authors [6,7], has not been confirmed by subsequent work. From the iron side, this structural diagram has been studied by Lamort [8], who distinguished the chemical compound  $TeFe_3$  corresponding to 22.2% Ti and having a melting point of 1400°. The presence of this compound has not been confirmed by more recent work [4,6].

At the present time, there is not just one opinion on the nature of the formation of the compound  $TiFe$ . Certain authors [4] assume that it is formed by a peritectic reaction at 1317° and 54% Fe; others [6] consider that the compound  $TiFe$  is stable only at high temperatures.

The present work was devoted to the problem of studying the structural diagram of this system in the regions of the compounds  $TiFe$  and  $TiFe_2$ , and also to the problem of establishing the boundaries limiting the solubility of titanium in iron. We studied the structural diagram of the system Ti-Fe by the methods of thermal, dilatometric, microstructural, and X-ray analyses and also by means of hardness and microhardness. The starting materials for the titanium-rich alloys were titanium hydride powder (99.2% Ti) and hydrogen-reduced iron (99.6% Fe). The preliminarily pressed and baked samples were melted under vacuum in a high-frequency furnace. The iron-rich alloys were fused from the same baked titanium and Armco iron. The cast alloys were subjected to thermal treatment according to the following regime: 100 hours at 1000°; 24 hours at 800°; 1000 hours at 550°; intermediate and final cooling was done in the furnace. Moreover, all alloys were studied after quenching from 800 and 1000°; and also, in determining the boundaries of the limiting solubility of titanium in iron, a series of alloys was quenched at 500, 800, 900, 1000, 1100, and 1200°.

In Figure 1 is presented the structural diagram of the system titanium-iron according to data from the investigation carried out by the above methods.

The structural diagram of the system was plotted by recording cooling curves on an N. S. Kurnakov pyrometer. Thermal analysis of the alloys was carried out by melting the samples in a high-frequency furnace in a stream of argon, using a platinum/platinum-rhodium thermocouple. In the present work, the presence of two metallic compounds was established,  $TiFe$  and  $TiFe_2$ , each of which melted with a clearly expressed maximum. The compound  $TiFe_3$  was not detected in the system titanium-iron. The melting points of  $TiFe$  and  $TiFe_2$  were found to be, respectively, ~1500 and 1480°. Our experimentally determined melting point for the compound  $TiFe$ , 1500°, agrees approximately with that predicted theoretically from a curve showing the change in melting point of metallic compounds of iron with elements of the periodic system [9]. The presence of the compounds  $TiFe$  and  $TiFe_2$  in the system requires the formation of three eutectics corresponding to the simultaneous crystallization of the phases:  $\beta+TiFe$ ,  $TiFe+TiFe_2$ , and  $TiFe_2+\alpha$ . The melting points of these eutectics are, respectively, 1100, 1280, and 1298°, and the eutectics correspond to the compositions 32, 62.5, and 82.5% Fe (the presence of these eutectics was clearly evidenced by the microstructural investigation of the alloys).

In the region of the chemical compound  $\text{TiFe}$ , breaks in the cooling curves were detected at temperatures below the melting point of  $\text{TiFe}$ , at approximately  $1340$ - $1360^\circ$ . We did not investigate this problem in detail, but it can be assumed that these breaks correspond to a polymorphic transformation of the compound  $\text{TiFe}$ . The temperature of the eutectoidal transformation  $\beta \rightarrow \alpha$  was determined by differential recording of the heating curves on an N. S. Kurnakov pyrometer. According to our data, it is  $615^\circ$ , and, according to literature sources, it is  $585$ - $600^\circ$  [3-5].

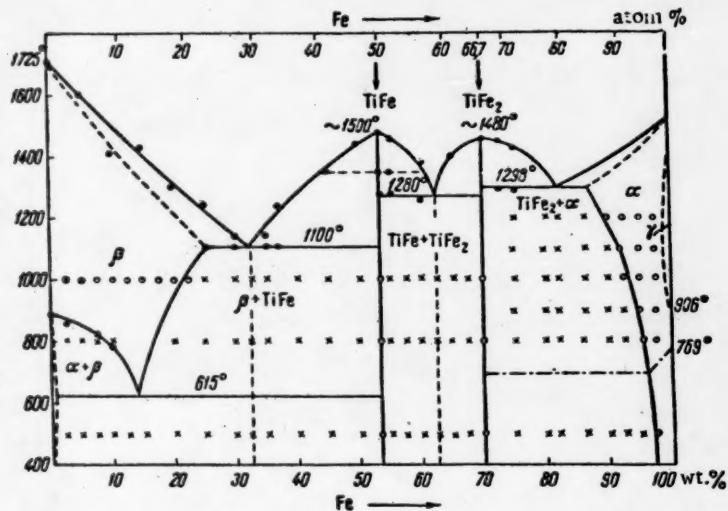


Fig. 1

Data from microstructural analysis agreed with the melting diagram for this system. The chemical compounds  $\text{TiFe}$  and  $\text{TiFe}_2$  correspond to the compositions 53 and 70 wt. % Fe, respectively. X-ray investigations of the tempered alloys confirmed the presence of the two metallic compounds  $\text{TiFe}$  and  $\text{TiFe}_2$  in the system titanium-iron. The absence of the compounds  $\text{Ti}_2\text{Fe}$  and  $\text{TiFe}_3$  in this system was shown by this same method.

Although the system titanium-iron has been studied by many authors, nevertheless, the question of the solubility of titanium in  $\alpha$ -Fe and its temperature dependence remains open. In connection with this, we studied the question in detail. The solubility of titanium in iron was studied by quenching at different temperatures. As a result of our investigations, the boundaries of the limiting solubility of titanium in  $\alpha$ -iron as it depends on temperature was established for the first time. At  $1200^\circ$ , the limiting solubility of titanium in iron, according to our data, is 12% Ti; at  $1100^\circ$ , it is 8.5% Ti; at  $1000^\circ$ , it is 7.5% Ti; at  $900^\circ$ , it is 5% Ti; at  $800^\circ$ , it is 4% Ti; and at  $500^\circ$ , it is 2.5% Ti.

The significant decrease in the solubility of titanium in iron (from 12 to 2.5% Ti) upon decreasing the temperature from  $1200$  to  $500^\circ$  predisposes these alloys to aging. The question of the hardening alloys of iron and titanium owing to dispersive disintegration of supersaturated solid solutions is of separate interest and requires further investigation.

A. A. Baikov Metallurgical Institute,  
Academy of Sciences of the USSR

Received December 16, 1955

#### LITERATURE CITED

- [1] W. Kroll, *Metaux Corrosion-Ind.*, 26, No. 313 (1951).
- [2] I. I. Kornilov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, No. 392 (1954) (T. p. 329)\*.

[2] H. W. Worner, J. Inst. Metals, 79, 173 (1951).

[4] W. I. Fretague, C. S. Parker and E. A. Peretti, U. S. Atomic Energy Commission Publictn., AFTR, 6597, 47 (1952).

[5] R. I. Van Thyue, H. D. Keessler and M. Hansen, Trans. Am. Soc. Metals, 44, 974 (1952).

[6] P. Duwes, J. K. Taylor, Trans. Am. Inst. Mining Engrs., 188, 1173 (1950).

[7] D. Polonis and I. G. Parr, J. Metals, 6, No. 10 (1954).

[8] I. Lamort, Ferrum, 11, 225 34 (1914).

[9] I. I. Kornilov, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 795 (1953) (T. p. 707)\*.

\* T. p. = C. B. Translation pagination

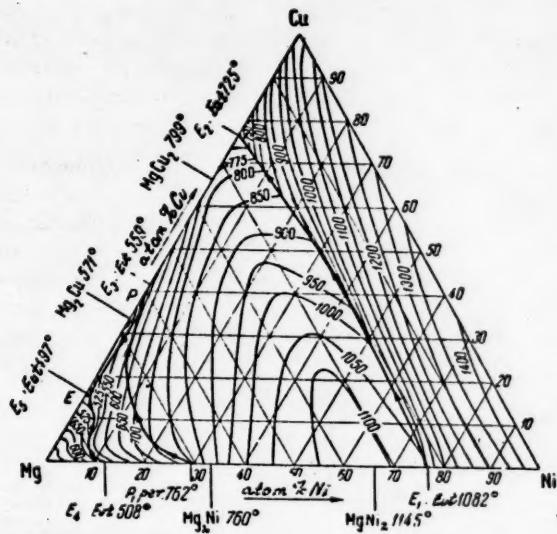


## MELTING DIAGRAM OF THE SYSTEM MAGNESIUM-COPPER-NICKEL

V. I. Mikheeva and G. G. Babayan

(Presented by Academician I. I. Chernyaev, January 24, 1956)

The melting diagram of the system magnesium-copper-nickel has been insufficiently studied. According to the data of Koester [1], which concerned only a small number of alloys, this diagram consists of only four areas of primary crystallization: magnesium, the compound  $Mg_2Ni$ , solid solutions formed by the compounds  $MgCu_2$  and  $MgNi_2$ , and solid solutions based on the binary system copper-nickel, separated by lines of co-crystallization of these phases. The invariant equilibrium point on the concentration triangular diagram was not determined in Koester's work.



According to the cooling curve data, the section  $\text{MgCu}_2$ - $\text{MgNi}_2$  (see Figure 2) corresponds to the crystallization of a continuous series of solid solutions formed by the compounds  $\text{MgCu}_2$  and  $\text{MgNi}_2$  (phase S), which was also confirmed by a study of the microstructure. It should also be noted that the structure of the series of alloys of this section was dendritic in nature, and this structure was not completely eliminated even by prolonged tempering at 475-500°. The area of homogeneity, encompassing the entire interval of concentrations between the compositions of the compounds  $\text{MgCu}_2$  and  $\text{MgNi}_2$ , was very narrow with respect to changes in magnesium content.

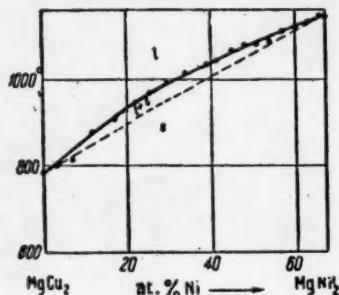


Fig. 2. Melting diagram of the section  $\text{MgCu}_2$ - $\text{MgNi}_2$ .

tion of 84.2 at. % Mg, 15% Cu, and 0.8% Ni; and P-transition point of the equilibrium  $\text{S} + 1 \rightleftharpoons \text{Mg}_2\text{Ni} + \text{Mg}_2\text{Cu}$  at a temperature of 540° and a composition of 65% Mg, 33.5% Cu, and 1.5% Ni.

The most interesting result of the present work was the confirmation of the existence of a homogeneous phase of solid solutions between the compounds  $\text{MgCu}_2$  and  $\text{MgNi}_2$ , at least at high temperatures, and, at the same time, the establishment of the possibility of the formation, within the boundaries of this phase and in the solid state, of a chemical compound similar to that found in the system magnesium-aluminum-zinc [2] and in a still more clearly expressed form in the system magnesium-copper-zinc [3]. In the latter system, the formation of the chemical compound  $\text{MgCuZn}$  was reflected on the melting diagram by a three-dimensional maximum in the binary section Mg-CuZn and by the clearly expressed synclinal trough of the area of magnesium crystallization.

In the present system, the proposed compound  $\text{MgCuNi}$  apparently possessed very little stability, and was not apparent in any of the elements of the ternary melting diagram except the isothermal area representing, in the present case, the magnesium area.

This especially clearly confirms the conclusion, which follows from the application of the law of mass action to the analysis of the form of the elements of the ternary composition-property diagram, that the formation of a low-stability compound is more susceptible to appearance on property isotherms in a region of weak solutions with respect to the solvent than in an area of phase crystallization with respect to the given compound.

N. S. Kurnakov Institute of General and  
Inorganic Chemistry, Academy of  
Sciences of the USSR

Received January 20, 1956

#### LITERATURE CITED

- [1] W. Koester, Z. Metallkunde, 11, 326 (1951).
- [2] V. I. Mikheeva and O. N. Kryukova, Proc. Acad. Sci. USSR, 50, 243 (1945).

- [3] V. I. Mikheeva and O. N. Kryukova, Bull. Dept. Phys.-Chem. Anal., 20, 76 (1950).
- [4] N. S. Kurnakova, Introduction to Physicochemical Analysis, 4th Ed., 1940, p. 68.
- [5] N. I. Stepanov, Prog. Chem., 5, 18 (1936).
- [6] V. I. Mikheeva , Bull. Dept. Phys.-Chem. Anal., 17, 174 (1949).



## INVESTIGATION OF ISOTOPE EXCHANGE BETWEEN HEAVY WATER AND SOME AQUOPOLY COMPOUNDS OF TUNGSTEN

Associate Member of the Academy of Sciences, USSR Vikt. I. Spitsyn and  
Yu. F. Berezhkina

Water is an important component part of aquopoly compounds of tungsten, and, in many of them, it determines their properties. Upon complete dehydration, these compounds decompose, being converted into anhydrous isopolytungstates characterized by different composition and structure. On the basis of a study of the rate of dehydration of sodium paratungstate,  $Na_{10}W_{12}O_{41} \cdot 28H_2O$ , the coordination formulas  $Na_5[H(W_2O_7)_5] \cdot 13.5H_2O$  [1],  $Na_5H_5[H_2(WO_4)_6] \cdot 10.5H_2O$ , or  $Na_{10}H_4[H_4(WO_4)_6] \cdot 24H_2O$  [2] have been proposed for it. The structure  $Na_6H_4[H_2(W_2O_7)_6] \cdot 27H_2O$  [3] has been ascribed to sodium metatungstate,  $Na_2W_4O_{14} \cdot 10H_2O$ .

The basic structural problem of aquopoly compounds is the distribution of water (or hydrogen ions) between the different spheres of the complex. This problem cannot be unequivocally solved by an investigation of the dehydration processes of the substances under consideration, since this method does not permit the study of the relative stability of the bonds of the different molecules of water or hydrogen atoms without partial or complete dehydration of the compounds.

For clarification of the natures of the bonds of the water, it is expedient to use the isotope exchange reaction between heavy water, which contains an admixture of  $D_2O$ , and the ordinary water of the aquopoly compounds, since replacement of hydrogen by deuterium, which does not cause dislocation of the water, permits estimation of the mobility of hydrogen in the complex.

We investigated isotope exchange of hydrogen and deuterium between water containing approximately 2.3 mole-%  $D_2O$  and various hydrates of sodium para- and metatungstate. These tungstates were prepared by electrolysis of  $Na_2WO_4$  solutions in a cell with a porous diaphragm. The anode liquid was subjected to evaporation and crystallization in a desiccator over sulfuric acid. The preparations thus obtained were analyzed for tungsten trioxide content by the hydroxyquinoline method. The bound water was determined in separate, weighed samples by calcination to constant weight. The sodium content was determined by separation of the  $Na_2SO_4$  from the filtrate from the precipitation of the tungsten, or it was calculated by difference. The analytical data are presented in Table 1.

The heavy water used for the isotope exchange experiments had an excess density of 2400-2800  $\gamma$ . A weighed sample of the aquopoly compound was introduced into a weighed amount of heavy water of known density. The mixture was maintained for a fixed time at constant temperature, after which the water was distilled from the solution and subjected to the standard purification. In view of the low solubility of sodium paratungstate, a solid phase was always present in the bottom of the reaction cell. Therefore, the solution was carefully decanted before distillation. Quantitative evaluation of the isotope exchange was carried out by measuring the density of the heavy water before and after the experiment. The density of the water was determined with a precision of 3  $\gamma$  by the flotation method using a hollow float [4]. In Table 2 are presented data on isotope

exchange between heavy water and the ordinary hydrate of sodium paratungstate.

TABLE 1

Compound		Content, %			Formula
		WO <sub>3</sub>	H <sub>2</sub> O	Na <sub>2</sub> O	
Sodium paratung-state	Found * Calculated	77.37 77.36	13.74 14.02	8.83 8.62	5.12Na <sub>2</sub> O·12WO <sub>3</sub> ·27.43H <sub>2</sub> O 5Na <sub>2</sub> O·12WO <sub>3</sub> ·28H <sub>2</sub> O
Sodium metatung-state	Found Calculated	79.58 79.30	14.68 15.40	5.74** 5.30	1.08Na <sub>2</sub> O·4WO <sub>3</sub> ·9.50H <sub>2</sub> O Na <sub>2</sub> O·4WO <sub>3</sub> ·10H <sub>2</sub> O

\* Average value for two analyses.

\*\* Na<sub>2</sub>O content of sodium metatungstate was calculated by difference.

TABLE 2

Isotope Exchange Between Heavy Water and the Paratungstate Na<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·27.43H<sub>2</sub>O. Temperature, 20°

Experiment No.	Composition of exchange mixture in g		Duration of the experiment, hours	Molecules of H <sub>2</sub> O entering into the exchange	Average
	Paratungstate	Heavy water			
1	2.93493	4.28970	2	11.7	
2	1.19260	7.16239	2	10.0	
3	2.00967	7.31270	2	11.4	
4	4.90522	6.73990	12	28.9	
5	4.96346	7.28052	12	27.5	
6	4.44144	7.61603	72	31.0	
7	5.07331	7.26508	72	26.2	

As seen from the results presented, the exchange of hydrogen between the water of the solvent and the water tied up in the sodium paratungstate proceeded at a high rate. After 2 hours, 40% of the water entering into the composition of the entire sample was exchanged, although, owing to the magnitude of the solubility of the paratungstate, the content of the salt in the liquid phase was only 20-25%. The mobility of the hydrogen was so great that exchange reached 100% after 12 hours. An increase in the duration of the experiments led to some increase in the magnitude of the exchange above that theoretically expected from the water content of the salt. Possibly, this phenomenon is connected with the enrichment of salt hydrates by heavy water, which is described in the literature [5].

The rate of exchange increased still more at 100°. After just 1 hour, an average of 17.5 molecules of water of the 28 in the hydrate were exchanged (Table 3).

The partially dehydrated sodium paratungstate hydrate, prepared at a temperature of 100° and having the composition Na<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·9.4H<sub>2</sub>O, did not exhibit a tendency toward exchange at room temperature conditions. Heating the solution to 100° made possible the exchange of 2.7 molecules of water (Table 3). Hydrates of paratungstate containing water in the amount of 4.3 and 2 molecules showed absolutely no exchange with heavy water.

Sodium metatungstate was used for the isotope exchange in the form of the usual decahydrate having, by analysis, the composition Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub>·9.5H<sub>2</sub>O (Table 1). Its ability to exchange with heavy water is more clearly expressed than is that of the paratungstate. At room temperature, 7-8 molecules of water possessed great mobility and exchanged almost instantaneously. However, the remaining 2-3 molecules of water exchanged far more slowly. Only after 336 hours were 9.3 molecules of water exchanged from the original hydrate (Table 4).

Complete exchange of water required heating the solution to 100° (Table 5).

TABLE 3

Isotope Exchange Between Heavy Water and Hydrates of Sodium Paratungstate Containing Different Amounts of Water. Temperature, 100°

Experiment No.	Initial hydrate	Composition of exchange mixture in g		Duration of experiment, hours	Molecules of H <sub>2</sub> O entering into the exchange	Av
		Paratungstate	Heavy water			
1		2.79782	8.21897	1	17.3	
2	5.12Na <sub>2</sub> O · 12WO <sub>3</sub> · 27.43H <sub>2</sub> O	2.63253	7.30012	1	16.9	
3		3.05186	7.08654	1	18.4	
4	5.12Na <sub>2</sub> O · 12WO <sub>3</sub> · 9.40H <sub>2</sub> O	1.73623	6.16031	1	2.5	
5		1.88310	5.03563	1	2.9	

TABLE 4

Isotope Exchange Between Heavy Water and Sodium Metatungstate, Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub> · 9.50H<sub>2</sub>O. Temperature, 20°

Experiment No.	Composition of exchange mixture in g		Duration of the experiment, hours	Molecules of H <sub>2</sub> O entering into the exchange	Average
	Metatungstate	Heavy water			
1	0.86189	5.99456	1	7.1	
2	1.85081	5.15554	1	9.1	
3	1.69152	5.94939	168	6.5	
4	3.08151	5.35909	168	7.7	
5	4.94181	8.57961	336	9.35	
6	4.51843	8.29535	336	9.30	

TABLE 5

Isotope Exchange Between Heavy Water and Sodium Metatungstate, Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub> · 9.50H<sub>2</sub>O. Temperature 100°

Experiment No.	Composition of exchange mixture in g		Duration of the experiment, hours	Molecules of H <sub>2</sub> O entering into the exchange	Average
	Metatungstate	Heavy water			
1	3.20025	7.90411	1	10.0	
2	3.32166	8.16585	1	9.2	

1.5 molecules of water in the partially dehydrated sodium metatungstate, Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub> · 4.1H<sub>2</sub>O, did not enter into the exchange. The mobility of hydrogen in the product of the further dehydration of sodium metatungstate, the product having the composition Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub> · 2H<sub>2</sub>O, was extremely low. A trifling exchange was observed only upon boiling. The most stably bound water in this hydrate, calculated on the basis of one molecule of Na<sub>2</sub>W<sub>4</sub>O<sub>13</sub>, was also approximately 1.5 molecules of H<sub>2</sub>O (Table 6).

The results of this investigation permit the conclusion that the distribution of water in the paratungstate anion is of such a nature that the deuterium easily penetrates to any molecule of bound water. The presence of two or three types of differently bound water, as required by the coordination formula, was not confirmed by the isotope exchange experiments. Partial elimination of water from the paratungstate led to a change in the structure of the anion such that not all molecules of the bound water were accessible to isotope exchange. It is possible that screening of the tungstate ions by the outer shell of the partially dehydrated anion plays a part here.

TABLE 6

Isotope Exchange Between Heavy Water and Partially Dehydrated Metatungstate,  $\text{Na}_2\text{W}_4\text{O}_{13} \cdot 2.0\text{H}_2\text{O}$ . Duration of the Experiment, 2 hours

Experiment No.	Composition of exchange mixture in g		Temp., °C	Molecules of $\text{H}_2\text{O}$ entering into the exchange	Average
	Metatungstate	Heavy water			
1	1.57842	6.27430	20	0	
2	1.78331	7.94821	20	0	
3	1.41952	3.49799	100	0.74	
4	1.45553	6.69765	100	0.44	$0.59 \pm 0.3$

In the metatungstate, apparently the inner part of the complex anion contains such a great number of tungstate ions that the bound water is difficultly accessible for exchange. However, a significant part of the water, approximately 70-80%, exchanges with deuterium practically instantaneously.

Institute of Physical Chemistry, Academy of Sciences of the USSR

Received February 11, 1956

#### LITERATURE CITED

- [1] H. Copaux, Bull. Soc. chim. Fr., [4], 13, 817 (1913).
- [2] A. Rosenheim, Z. anorg. allg. Chem., 96, 139 (1916); A. Rosenheim and A. Wolff, Z. anorg. allg. Chem., 193, 47 (1930).
- [3] H. Copaux, Z. anorg. Chem., 74, 351 (1912).
- [4] A. I. Brodsky, The Chemistry of Isotopes, 1951, p. 44.
- [5] J. N. E. Day, E. D. Hughes et al., J. Chem. Soc., 1934, 1593.

## PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

Section: CHEMISTRY

Volume 108, Issues 1-6

May-June, 1956

## TABLE OF CONTENTS

	Page	Issue	Russian Page
1. Synthesis of Alkylacetoxepoxysilanes. <u>Associate Member of the Academy of Science USSR K. A. Andrianov and V. G. Dubrovina</u> . . . . .	207	1	83
2. Grignard Reactions with Some Unsaturated Ketones Containing a Furan Nucleus. <u>B. N. Dashkevich and S. S. Zhuder</u> . . . . .	211	1	87
3. The Relation Between the Structure and Certain Properties of a Series of Azo Dyes Containing Amide Groups. <u>B. M. Krasovitsky, R. M. Matskevich and T. M. Nikishova</u> . . . . .	215	1	91
4. Synthesis of Isopropylnaphthalene and Secondary Butylnaphthalene by the Alkylation of Naphthalene with Olefins. <u>Academician A. V. Topchiev, Ya. M. Paushkin and M. V. Kurashev</u> . . . . .	219	1	95
5. The Structure of Agar-Agar Gel. <u>V. I. Sharkov and R. K. Boyarskaya</u>	223	1	99
6. Certain Regularities During the Thermal Chlorination of n-Dodecane. <u>R. S. Galanina and A. S. Nekrasov</u> . . . . .	227	2	251
7. Verification by Means of Tagged Alcohol, of the Dehydration-Condensation Mechanism of the Formation of Hydrocarbon Chains in the Synthesis of Hydrocarbons From CO and H <sub>2</sub> . <u>O. A. Golovina, Associate Member of the Academy of Science USSR S. Z. Roginsky, M. M. Sakharov and Ya. T. Eidus</u> . . . . .	229	2	253
8. The Effect of Anions of the Outer Sphere on the Nature of Substitution Into the Inner Sphere of Complex Compounds. <u>Associate Member of the Academy of Science USSR A. A. Grinberg and Kh. I. Gildengershel</u> . . . . .	233	2	256
9. The Question of the Mechanism of Vulcanization Accelerators. Reaction of Mercaptobenzothiazole with Sulfur. <u>B. Dogadkin and I. Tutorsky</u> . . . . .	237	2	259
10. A Thermally Stable Variety of Aluminum Hydroxide. <u>I. V. Krotov</u> . . . . .	241	2	263
11. Relative Reactivity of the C-Cl Bonds of $\alpha$ - and $\gamma$ -Chloroalkyltrimethylsilanes in the Reaction with Potassium Iodide. <u>V. F. Mironov</u> . . . . .	245	2	266
12. Acidity Function of the System H <sub>2</sub> SO <sub>4</sub> -HSO <sub>3</sub> Cl. <u>V. A. Palm</u> . . . . .	249	2	270
13. Synthesis and Properties of Polyhydric Phenols. <u>P. I. Sanin and A. V. Ulyanova</u> . . . . .	253	2	274
14. Observation of the Reactions of Formation of MgAl <sub>2</sub> O <sub>4</sub> and BeAl <sub>2</sub> O <sub>4</sub> by Means of Luminescence Spectra. <u>A. K. Trofimov</u> . . . . .	257	2	277
15. Investigations in the Field of the Synthesis and Transformations of Oxygen-Containing Organosilicon Compounds. Synthesis of Organosilicon Acetals Based on the Vinyl Ether of $\gamma$ -Hydroxypropyltrimethylsilane, Organosilicon Alcohols, and Silanol. <u>I. A. Shilkhiev and N. V. Komarov</u> . . . . .	261	2	279

## PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

May-June, 1956

## TABLE OF CONTENTS

(continued)	Page	Issue	Russian
	Page	Page	Page
16. The Role of Copper in the Reaction Between Ethyl Chloride and Silicon. Associate Member of the Academy of Science USSR K. A. Andrianov, S. A. Golubtsov, I. V. Trofimova, A. S. Denisova and R. A. Turetskaya . . . . .	265	3	465
17. Alkylation of Meta-, Ortho-, and Para-Cresols with Acetylene. V. L. Vaiser and A. M. Polikarpova . . . . .	269	3	469
18. Isomerization of Monoolefinic Hydrocarbons by the Action of Calcium Amide. I. V. Gostunskaya, N. I. Tyunkina and Academician B. A. Kazansky . . . . .	273	3	473
19. The Question of the Quantitative Characterization of the Trans-Effect in Complex Compounds of Tetravalent Platinum. O. E. Zvyagintsev and E. F. Karandasheva . . . . .	277	3	477
20. Organoboron Compounds: Synthesis of Trialkylboron Compounds From Esters of Dibutylboric Acid. B. M. Mikhailov and T. A. Shchegoleva . . . . .	281	3	481
21. Photochlorination of Diethyldichlorosilane in the Liquid State. E. P. Mikheev . . . . .	285	3	484
22. The Question of the Mechanism of the Chlorination of Arylsulfonic Acids With Chlorosulfonic Acid. Chlorination of p-Phenylurethylsulfonic Acid. V. A. Palm . . . . .	289	3	487
23. Study of Isotope Exchange Between Gaseous Oxygen and Alkali Metal Sulfates at High Temperature. Associate Member of the Academy of Sciences, USSR Vikt. I. Spitsyn and V. G. Finikov . . . . .	293	3	491
24. Kinetics of the Spontaneous Decomposition of Potassium Ozonide. Associate Member of the Academy of Science USSR I. A. Kazarnovsky, S. I. Raikhshtein and L. N. Bykova . . . . .	297	4	641
25. Polymorphism of Rubidium and Cesium Nitrates and Their Interaction With Barium Nitrate. V. E. Plyushchev, I. B. Markina and L. P. Shklover . . . . .	301	4	645
26. The Reaction of Unsymmetrical Organic $\alpha$ -Oxides With Acetone in the Presence of Boron Fluoride. F. G. Ponomarev . . . . .	305	4	648
27. The Preparation of Complex Compounds of Tetravalent Platinum With Five and Six Different Substituents in Trans-And Cis-Configurations. L. N. Essen and A. D. Gelman . . . . .	309	4	651
28. The Reduction of Selenium Dioxide, Dissolved in Sulfuric Acid, by Sulfur Dioxide. A. G. Amelin and E. V. Yashke . . . . .	313	5	849
29. Investigation of the Resin From the Roots of Ferula Gumosa Boiss. G. V. Pigulevsky and T. N. Naugolnaya . . . . .	317	5	853
30. Alkaloids of the Siberian Moonseed (Menispermum Dauricum). T. N. Ilyinskaya . . . . .	321	6	1081
31. Structural Diagram of the System Titanium-Iron. I. I. Kornilov and N. G. Boriskina . . . . .	323	6	1083

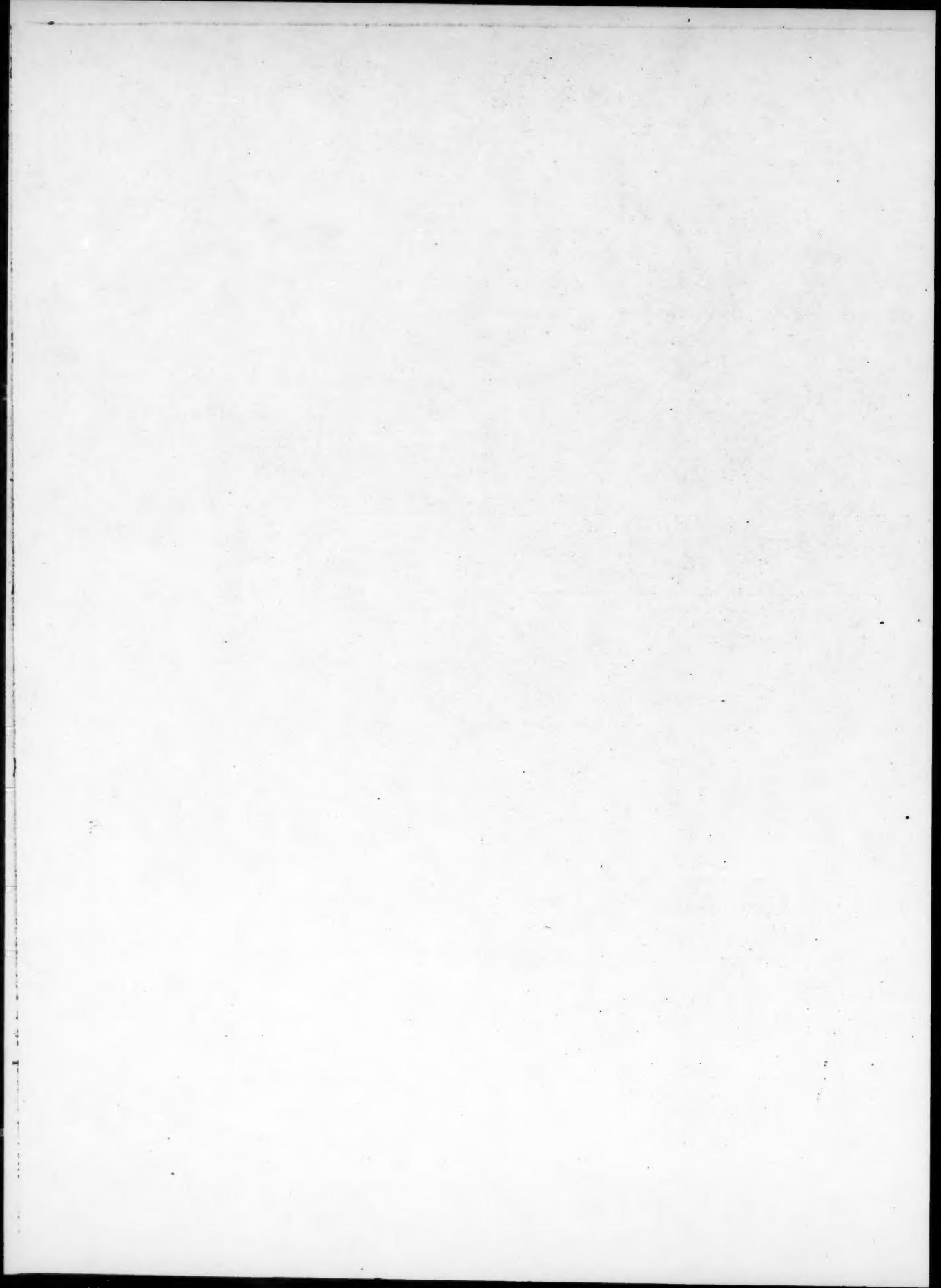
## PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

May-June, 1956

## TABLE OF CONTENTS

(continued)

		page	Issue	Russian Page
32. Melting Diagram of the System Magnesium-Copper-Nickel. <u>V. I.</u> <u>Mikheeva and G. G. Babayan</u> . . . . .	327	6	1086	
33. Investigation of Isotope Exchange Between Heavy Water and Some Aquopoly Compounds of Tungsten. <u>Associate Member of the Academy of Science</u> <u>USSR Vikt. I. Spitsyn and Yu. F. Berezkina</u> . . . . .	331	6		1088



**CONSULTANTS BUREAU COMPLETE SUBSCRIPTION  
TRANSLATIONS OF SOVIET JOURNALS FOR 1957**

Price quoted covers complete translation of all issues, plus comprehensive cross index.  
(\*) indicates that this journal will be published in English translation for the first time  
in 1957.

**BIOLOGY AND MEDICINE**

Biochemistry (Biokhimiya. 6 issues per year) .....	\$ 20.00 per year
Bulletin of Experimental Biology and Medicine (12 issues per year) .....	20.00
*Biochemistry Section of Proc. Acad. Sci. USSR (Doklady. 36 issues per year, to be published in 6 issues) .....	65.00

**CHEMISTRY, PURE AND APPLIED**

Journal of General Chemistry of the USSR (Obozrhei Khimii. 12 issues, 3600 pp) .....	170.00
Journal of Analytical Chemistry of the USSR (6 issues) .....	80.00
Journal of Applied Chemistry of the USSR (Prikladnoi. 12 issues) .....	95.00
Bulletin of the Acad. Sci. USSR, Div. Chem. Sci. (Izvestiya. 12 issues) .....	150.00
Chemistry Sections of Proc. Acad. Sci. USSR (Doklady. 36 issues per year, to be published in 6 issues).	
Chemistry Section .....	95.00
Chemical Technology Section .....	15.00
Agrochemistry Section .....	15.00
Geochemistry Section .....	15.00
All four sections of Proc. Acad. Sci. cited above may be purchased as a unit for only .....	125.00
*Physical Chemistry Section of Proc. Acad. Sci. USSR (Doklady. 36 issues, to be published in 6 issues) .....	160.00

**PHYSICS**

The Soviet Journal of Atomic Energy (12 issues per year) .....	75.00
Supplements to J. Atomic Energy — prices to be announced.	
*Applied Physics Sections of Proc. Acad. Sci. USSR (Doklady. 36 issues, to be published in 6 issues. Includes all reports on: biophysics, crystallography, electrotechnics, hydraulics, hydro- mechanics, mechanics, mineralogy, theory of elasticity) .....	200.00

**ELECTRONICS**

Automation and Remote Control (Avtomatika i Telemekhanika. 12 issues) .....	185.00
Colloid Journal (J. Expt. and Theoretical Physics and Chemistry of Colloids. 6 issues) .....	80.00
*Geological Sciences Section, Proc. Acad. Sci. USSR (Doklady. 36 issues, to be published in 6 issues) .....	200.00
Cement (6 issues) .....	60.00
Glass and Ceramics (12 issues) .....	80.00
*Metallurgist (12 issues) .....	95.00

These complete Consultants Bureau translations, by scientists for scientists, include all tabular material and diagrams integral with the text. Each issue of each translation is mailed to subscribers upon publication.

Direct your orders to:



**CONSULTANTS BUREAU, INC.**

227 WEST 17TH STREET, NEW YORK 11, N. Y. ALGONQUIN 5-0713



